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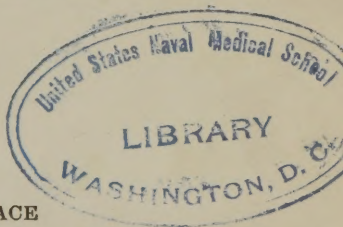
OUTLINES

OF THE COURSE OF

QUALITATIVE ANALYSIS

FOLLOWED IN THE GIESSEN LABORATORY.

BY

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WITH A PREFACE
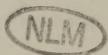
By BARON LIEBIG.

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PREFACE

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THE course of instruction in Chemical Analysis pursued at Giessen has been adopted in Great Britain and throughout Europe. The last edition of the " Qualitative Analysis," by Fresenius, a former assistant of Baron Liebig, was simultaneously published in German, French, and English. This circumstance, in connection with the fact that four German editions of it have already been sold, shows at the same time the demand for chemical knowledge, and the excellence of the method of instruction.

Dr. Will, now Professor Extraordinary in the University at Giessen, has for many years been an assistant of Baron Liebig, being at first associated with him in his private laboratory, and in giving instruction in practical chemistry ; but more recently, in consequence of the increase of the school, he has taken the direction of a separate laboratory. His long experience has eminently qualified him for the task of preparing a text-book, and the volume appearing under his name, presents in compact form and arrangement, the course introductory to that of the " Hundred Bottles."

These consist of solutions and solids, without labels, whose chemical contents are to be ascertained. Before entering upon their examination, the student has, with the aid of a text-book and a teacher, become more or less familiar with the reactions of the bases, acids, and elementary bodies of which they are composed, but only in their isolation ; he now comes to recognize them in their combinations, and in the presence of other bodies tending to obscure their reactions. This calls

into exercise all his previous acquisitions. The contents of the bottles become more and more complex as he advances from 1 to 100. In the first ten solutions he seeks only an acid; in the second ten, perhaps only a base. The next twenty are solids, and both an acid and a base are to be sought in each bottle. Then occur bottles, each containing several bases, and then others, each containing several acids; and thus increasing, till the last ten of the hundred may be found to contain from ten to twenty ingredients. The progressive development of the taste and capacity for chemical analysis, and of the love of order and neatness, which this system secures, make acquisition and instruction grateful.

At the conclusion of this course, pharmaceutical preparation and determinations in quantitative analysis commence. The operator has become expert in manipulation; he has acquired patience and perseverance for repetition where doubt existed, has gained confidence in the reagents; and the most important qualification to the young analyst, conscientiousness in attending faithfully to the minutest details upon which a result may depend, has been developed.

Such is, in general, the elementary course at Giessen, and more or less in all the prominent schools of chemistry throughout Europe.

The text-book of Professor Will was translated into English for the immediate use of the Royal College of Chemistry recently established in London, under the direction of Professor Hoffman. Its chief advantages are its compact and systematic arrangement, and its adaptation to the successive wants of the student, who is led by it to the constant exercise of his acquisitions. It has been adopted in the University at Cambridge, in the United States.

CAMBRIDGE LABORATORY, September 1, 1847.

PREFACE.

In order to benefit by a course of practical instruction in chemical analysis, the student must necessarily obtain a preliminary acquaintance with the general principles and theories of the science.

The present work is designed for use in the laboratory; consequently everything which does not immediately refer to the processes of analysis is very properly excluded. If we consider, as we ought, the main design of practical instruction in a chemical laboratory, to be the exercise of reflection and judgment in order to a profound understanding of the scientific bases upon which the separation of bodies from each other depends, it is obvious that a work adapted for laboratory use must differ from one designed for self-instruction. In books of the latter kind, it must be assumed that the reader has no previous knowledge; they must therefore include a description of a multitude of things not absolutely relevant to their professed object: with some of these the student ought to become acquainted by attendance on lectures, or by reading an elementary work on the science, such as the preparation of reagents; with others, (apparatus and instruments,) he becomes familiar immediately upon his entering the laboratory. Those therefore

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must be considered the best of books of this kind, which
most completely supersede the necessity of a teacher ; and
necessarily, on this ground, the great advantages derived
from oral instruction, and the excitement of the student's
own power of observation and reflection, are sacrificed to
the mere mechanical course of operations, which leads
securely to the detection of individual bodies.

The want of an introduction to chemical analysis, adapted
for the use of a laboratory, has given rise to the present
work, which contains an accurate description of the course
I have followed in my laboratory with great advantage for
twenty-five years. It has been prepared at my request by
Professor Will, who has been my assistant during a great
part of this period. I hope and believe that it will be
acceptable to the English public.

<div align="right">JUSTUS VON LIEBIG.</div>

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OUTLINES

OF

QUALITATIVE ANALYSIS.

SECTION I.

BEHAVIOR OF THE METALS AND THEIR OXIDES WITH REAGENTS.

GROUP I.

THE ALKALI-METALS.

Potassium, Sodium, [Lithium], Ammonium.

The metals of this group are lighter than water, which they decompose at the common temperature, with disengagement of hydrogen; their compounds with *chlorine, bromine, iodine, sulphur,* and *oxygen* are soluble in water, as also are the combinations of their oxides with most acids, particularly with *sulphuric acid* HO, SO_3, *nitric acid*, HO, NO_5, *phosphoric acid*, 3 HO, PO_5, and *carbonic acid*, CO_2. The most important reactions

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of the salts of the alkali-metals, by which they may be easily recognised, and qualitatively separated, are the following : —

a. POTASSA.
KO.

Bi-chloride of platinum Pt Cl$_2$ produces in moderately dilute potassa-salts, especially on the addition of some hydrochloric acid H Cl and alcohol, an orange-yellow crystalline precipitate, which is a double salt of chloride of potassium and bi-chloride of platinum K Cl, Pt Cl$_2$.

Tartaric acid 2 HO, C$_8$ H$_4$ O$_{10}$ = 2 HO, $\overline{\text{T}}$, also gives a white crystalline precipitate, appearing sooner or later according to the concentration of the liquid. This precipitate,— bitartrate of potassa KO, HO, $\overline{\text{T}}$ is soluble in 60 parts of water, and dissolves readily in strong mineral acids and alkaline liquids.

Potassa-salts not containing soda, impart to the exterior blowpipe flame a distinct *violet* tint; the same color is produced in the flame of alcohol, when mixed with a moderately dilute solution of a potassa-salt.

b. SODA.
Na O.

Soda (even in the presence of the other two fixed alkalies) is recognised by its salts imparting an intense *yellow* color to the exterior blowpipe flame.

Since soda forms generally soluble compounds with acids, we possess very few reagents, which separate it from its solution in an insoluble state.

Carefully prepared *antimoniate of potassa* KO, Sb O$_5$ produces a white precipitate of antimoniate of soda Na O, Sb O$_5$ in a moderately dilute solution of a neutral or at least only slightly alkaline soda-salt. Before

employing this reagent, we must carefully ascertain, that no alkaline earth or other oxide is present in the solution to be examined.

c. [LITHIA.]
Li O.

Lithia-salts are recognised by imparting a beautiful *crimson* to the exterior flame, when exposed on a platinum-wire to the point of the inner blowpipe flame. The presence of soda renders this imperceptible, on account of its characteristic yellow flame.

When a clear solution containing lithia is evaporated to dryness in the presence of *phosphate of soda* 2 Na O, HO, PO_5, and *carbonate of soda* NaO, CO_2, there remains after treatment with water a not readily soluble crystalline double-salt 2 NaO, PO_5 + 2 LiO, PO_5, which produces a transparent mass when fused together upon platinum-foil with carbonate of soda.

d. AMMONIA. (OXIDE OF AMMONIUM).
NH_4 O.

Ammonia gives with *bi-chloride of platinum* and with *tartaric acid* the same reactions as potassa; the precipitates have also a similar composition.

Ammonia is recognised with ease and certainty, even in the presence of all the other bases, by its being set free in a gaseous state by the action of the caustic alkalies, or the alkaline earths, upon its compounds. For this purpose we generally use *hydrate of lime* HO, CaO. Ammonia in the state of gas is distinguished by its peculiar smell, and by the white clouds which are formed, when a glass-rod moistened by hydrochloric

acid (not fuming) is brought near the liquid to be examined. This appearance is owing to the formation of chloride of ammonium NH_4Cl.

GROUP II.

THE METALS OF THE ALKALINE EARTHS.

Barium, Strontium, Calcium, Magnesium.

The metals also of this group, so far as they are known, decompose water without the presence of an acid; their compounds with *oxygen* and *sulphur* are soluble in water, though less so than those of the alkali-metals. *Oxide of magnesium* (*magnesia*) is almost insoluble in water. *Baryta, strontia, lime,* and *magnesia,* form compounds with *carbonic* and *phosphoric acids,* which are insoluble in water; these oxides are, therefore, precipitated from their neutral solutions by the soluble and neutral salts of these acids. (This constitutes the distinction between the first and second group.)

Their sulphates exhibit a very unequal degree of solubility in water.

Sulphate of baryta is insoluble.

Sulphate of strontia nearly so.

Sulphate of lime is slightly soluble.

Sulphate of magnesia is very soluble.

a. BARYTA.
Ba O.

The salts of baryta (which are soluble in water) are not precipitated by *ammonia.*

Carbonate of potassa, carbonate of soda, and *carbo-*

nate of ammonia, (the latter, on addition of some pure ammonia and a slight increase of temperature), precipitate this base completely in the form of carbonate, BaO, CO_2.

Baryta is likewise thrown down completely in the form of sulphate BaO, SO_3, from all its salts, as well those soluble in water, as those in acids, either by free *sulphuric acid*, or by any of the *soluble sulphates.* Even *sulphate of lime* CaO, SO_3 decomposes soluble baryta-salts by the formation of sulphate of baryta, which is insoluble both in alkalies and acids.

Hydro-fluosilicic acid HF, SiF_2 produces in neutral and acid solutions of baryta an almost transparent precipitate of silico-fluoride of barium BaF, SiF_2, which, therefore, is only to be distinctly recognised after it has become deposited.

Phosphate of soda gives with neutral salts of baryta a precipitate of phosphate of baryta, which is easily soluble in acids, even in acetic acid.

Most of the baryta-salts impart a *yellowish-green* color to the flame of alcohol.

b. STRONTIA.
Sr O.

Salts of strontia much resemble in their chemical character the compounds of baryta.

The sulphate of strontia is not so completely insoluble in water and acids as the sulphate of baryta. The precipitate of sulphate of strontia produced by sulphate of lime or other soluble sulphates, therefore, does not appear immediately, unless the solution be very concentrated.

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Hydro-fluosilicic acid gives no precipitate with solutions of strontia.

Strontia salts impart a *crimson* color to the flame of alcohol.

Strontia, when in company with baryta, is detected by dissolving the carbonates in hydrochloric acid, evaporating to dryness, and digesting the residue with *strong alcohol.* Chloride of strontium is dissolved, and may be recognised in this solution either by sulphuric acid, or the color of the flame, &c.

c. LIME.
Ca O.

Lime is distinguished from baryta and strontia by its not giving a precipitate with *dilute sulphuric acid*, sulphate of lime being somewhat soluble in water, and in acids.

Neutral salts of lime (even a solution of the sulphate) are precipitated completely by *oxalic acid* HO, $C_2O_3 =$ HO, $\overline{O}$, or the *soluble oxalates*, which affords the best method for detecting lime. When the three are together, baryta and strontia are precipitated by *dilute sulphuric acid*, or *sulphate of potassa*, the filtrate being neutralised with ammonia; the lime is then precipitated by oxalic acid. Oxalate of lime is insoluble in *acetic acid*, but soluble in mineral acids.

Several lime-salts, as chloride of calcium, and nitrate of lime, are soluble in strong alcohol, and impart a *yellowish-red* color to its flame.

Sulphate of lime is insoluble in alcohol, (even when it is dilute); therefore, sulphuric acid precipitates lime completely from solutions of its salts in alcohol.

d. MAGNESIA
Mg O.

From the three alkaline earths above mentioned, magnesia is distinguished by its *sulphate* being very soluble in water.

When in company with ammonia, magnesia is precipitated *only* by *soluble phosphates.*

When no ammonia, or ammoniacal salts are present, soluble salts of magnesia are thrown down completely by the fixed *caustic alkalies*, as hydrate, HO, Mg O, on boiling also by their *neutral carbonates*, as a compound of hydrate and carbonate 2 (HO, Mg O) + 3 (Mg O, CO₂.)

Ammonia precipitates them only partially as hydrate, a soluble double salt being formed at the same time.

Soluble magnesia-salts are not precipitated in the cold by *bicarbonate of ammonia*, and only partially and slowly by *carbonate* and *sesqui-carbonate of ammonia ;* the precipitate obtained by the latter reagents, appears quicker and more completely on ebullition.

All these precipitates are redissolved on the addition of a sufficient quantity of chloride of ammonium. But, as already mentioned, the precipitate, which in the presence of ammonia is produced by *phosphate of soda*, (this precipitate is a tribasic phosphate, 2 MgO, NH₄O, PO₅ + 12 aq), remains insoluble even in a very great excess of chloride of ammonium.

When magnesia-salts are heated upon charcoal before the blowpipe, moistened with a drop of *solution of nitrate of cobalt*, CoO, NO₅ and ignited again powerfully, for a short time, the salt assumes a *pale red* color.

But this is not always perceptible, when other oxides are present.

Magnesia may, therefore, be separated from baryta, strontia, and lime, simply by *carbonate of ammonia*, in the presence of chloride of ammonium and ammonia. Magnesia remains in solution, while the three other earths are completely precipitated (especially on a slight increase of temperature and addition of some ammonia). The filtrate may then be tested for magnesia with *phosphate of soda.*

In order to detect the fixed alkalies when in conjunction with magnesia, it is necessary to get rid of the magnesia and all the ammoniacal salts. This is effected by evaporating the solution and igniting. The residue is then heated with water, a *solution of baryta* (or, what is equally good, *sulphide of barium,* Ba, S), added to the liquid as long as a precipitate is formed. The excess of baryta, after filtration, is then separated either by *sulphuric acid,* or *carbonate of ammonia,* and the residue obtained by evaporating the filtrate, ignited.

This residue must now be tested for potassa, soda [and lithia], as above explained. When, however, the solution to be examined contains no ammoniacal salts, the first evaporation and ignition may of course be omitted, since then the magnesia may be completely precipitated by caustic baryta. If the second evaporation leaves no residue, there are of course no alkalies in the solution.

The salts of the alkaline earths which are soluble in water, are *not* precipitated by *ammonia* or *sulphide of ammonium* NH₄ S, (magnesia excepted, *which is pre-*

cipitated by the former reagent, when a sufficient quantity of an ammoniacal salt be present) ; those, however, which are insoluble in water but soluble without decomposition in acids, are precipitated, such as the compounds of the alkaline earths with *phosphoric, arsenic* AsO_5, *hydro-fluosilicic* and *boracic* BO_3 acids, also *oxalic* acid, and many other non-volatile organic acids.   This applies to the compounds of lime with almost all the above-mentioned acids, but in the case of magnesia only to the phosphate.   These salts, when dissolved in an acid, fall down as salts by neutralising with ammonia, or (what is the same) with sulphide of ammonium.

They exhibit the same behavior with the common reagents as the earths themselves ; especially they are insoluble in potassa.   When in testing for acids we find any of the above (which are principally non-volatile acids), these properties must be borne in mind, in order that we may not overlook the alkaline earths.   When the acid combined with the alkaline earth is *oxalic*, or any other organic acid, the precipitate after ignition effervesces on the addition of a mineral acid ; in this case the base after being dissolved in hydrochloric acid is no more precipitated by ammonia, and may be recognised in the usual manner.   When the acid is *phosphoric* the precipitate is not decomposed by ignition; in order to detect the base, acetate of potassa $K O$, $\overline{A}$ is added to the solution of the salt in hydrochloric acid, and the liquid tested with *oxalate of ammonia*, on the one hand (*lime*), and *sulphate of lime* on the other (*baryta, strontia*).   *Magnesia* remains in solution (baryta, strontia and lime being separated), and is detected by

saturating with ammonia, and addition of phosphate of soda.

GROUP III.

METALS WHICH ARE NOT PRECIPITATED BY HYDROSUL-
PHURIC ACID FROM THEIR SOLUTIONS CONTAINING
FREE MINERAL ACID, BUT WHICH ARE THROWN DOWN
BY SULPHIDE OF AMMONIUM, PARTLY AS OXIDES, PART-
LY AS SULPHIDES, FROM THEIR NEUTRAL SOLUTIONS.

This great group consists of the following fifteen metals :

Aluminum, [*glucinum, thorium, yttrium, cerium, zir-conium*] *chromium*, [*titanium, tantalum**] *manganese, iron, zinc*, [*uranium*] *cobalt* and *nickel*.

The oxides of the nine first mentioned metals do not give up their oxygen for the sulphur of the hydrosulphuric acid HS; they are thrown down therefore as oxides by the action of the ammonia contained in the sulphide of ammonium with evolution of hydrosulphuric acid, ex. gr.

$$Al_2O_3,3SO_3 + 3NH_4S' + 3HO = AL_2O_3 + 3(NH_4O,SO_3) + 3HS.$$

These are, with the exception of chromium, [titanium and tantalum] the earths proper. The oxides of the last six metals are decomposed in their neutral solutions by the action of hydrosulphuric acid, water being formed, and a sulphide insoluble in water, ex. gr.

$$Mn O, S O_3 + H S = Mn S + H O, S O_3.$$

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* We might add to these *lanthanum*, and *didymium*, *erbium*, and *terbium*, which respectively resemble *cerium* and *yttrium*, also *niobium*, which was formerly mistaken for *tantalum*. We have omitted these, as their chemical reactions are not yet sufficiently known.

These metals decompose water in the presence of acids, with evolution of hydrogen; their sulphides disengage, under the same circumstances, hydrosulphuric acid : sulphide of nickel, and sulphide of cobalt, however, are only with difficulty soluble in dilute mineral acids.

In consequence of their behavior with the common reagents, the oxides and sulphides of the metals of this group may be arranged under the following subdivisions.

1. [Oxides which are either quite insoluble in hydrochloric acid, or which may by boiling be precipitated from their acid solution : *titanic acid, tantalic acid.*]

2. Sulphides which are insoluble, or soluble with great difficulty in dilute hydrochloric acid : *sulphide of nickel* and *sulphide of cobalt.*

3. Oxides which are not precipitable by ammonia after addition of chloride of ammonium to their solution : *oxides of nickel, cobalt, zinc, iron* and *manganese.*

4. Oxides which, in the absence of ammoniacal salts, are precipitated by the fixed caustic alkalies, and which are insoluble in an excess of the precipitant : *oxide of nickel* and of *cobalt, oxide* and *peroxide of iron, oxide of manganese,* [*sesquioxide of uranium, oxide* and *sesquioxide of cerium, yttria, zirconia.*]

5. [Oxides soluble in the fixed caustic alkalies, and in carbonate of ammonia : *glucina.*]

6. [Oxides insoluble in the alkalies but soluble in carbonate of ammonia : *peroxide of uranium, oxide* and *sesquioxide of cerium, yttria, thorina* and *zirconia.*]

7. [Oxides which are precipitated from their acid solutions by sulphate of potassa KO, SO_3 in the form of a double salt: *oxide* and *sesquioxide of cerium, zirconia, thorina, yttria.*]

These peculiarities form the basis of the qualitative analysis of this group, the details of which are explained below.

The special behavior of the individual members of this group with reagents, which affords us the means of confirming the presence of one or other of them, is as follows :—

I. — METALS WHICH ARE PRECIPITATED BY SULPHIDE OF AMMONIUM AS OXIDES.

1. *Soluble in Potassa.*

ALUMINA, [GLUCINA,] AND SESQUIOXIDE OF CHROMIUM.

a. ALUMINA.

$$Al_2 O_3.$$

Alumina forms with acids colorless salts, which for the most part are soluble in water, have an acid reaction, and lose their acid by ignition, if it be volatile.   Most compounds of alumina insoluble in water, may be dissolved in acids; the natural aluminates, undecomposable by acids, are decomposed by fusion with the alkaline carbonates, or with *bisulphate of potassa*, $KO, SO_3 + HO, SO_3$ by which the alumina is rendered soluble in acids.

Fixed caustic alkalies throw down from solutions of alumina in acids, basic salts, as gelatinous precipitates, which redissolve in excess of alkali.   The alumina may

be again completely precipitated from its alkaline solution, on addition of chloride of ammonium, or better, by neutralising with hydrochloric acid and adding ammonia.

The *alkaline carbonates* and *ammonia* (the former with evolution of carbonic acid) precipitate alumina from its solutions in the form of hydrate, $_3HO, Al_2 O_3$; this precipitate is soluble in a concentrated solution of *carbonate of soda*, it is very little soluble in *caustic ammonia*, and less so in *carbonate of ammonia*.

Phosphate of soda precipitates alumina from its slightly acid solutions as a phosphate, which comports itself with acids and alkalies like pure alumina.

When *silicate of potassa* (soluble glass) is added to a solution of alumina or phosphate of alumina in caustic potassa, a precipitate of silicate of alumina is formed; in the latter case phosphoric acid remains in solution.

On heating an alumina-salt before the blowpipe, moistening with *cobalt solution*, and again igniting strongly, the mass assumes a beautiful *blue* color.

b. [GLUCINA.]
Be O.

Glucina comports itself with almost all reagents like alumina; it is however distinguished from alumina by its being precipitated from its solution in dilute potassa by continuous boiling, and by its solubility in alkaline carbonates.   Nevertheless these carbonates first produce a voluminous precipitate of carbonate of glucina, which then dissolves in a great excess of the precipitant.   *Carbonate of ammonia* dissolves the hydrate and

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the carbonate of glucina more readily than the fixed alkaline carbonates, from which solution the earth is reprecipitated by boiling.

When moistened with *cobalt-solution* and ignited, the salts of glucina yield a *grey* mass.

c. SESQUIOXIDE OF CHROMIUM.

$$Cr_2 O_3.$$

Sesquioxide of chromium, after ignition, is almost insoluble in acids, but when freshly precipitated, or dried only at a gentle heat, it is easily soluble in acids. The salts are beautifully green or violet under reflected, but appear red by transmitted, light; those which are not soluble in water dissolve easily in hydrochloric acid.

Ammonia precipitates from the solutions of this oxide a bluish-green hydrate $3 HO, Cr_2O_3$, which dissolves to a small amount in strong ammonia, forming a pink solution.

Carbonate of ammonia produces the same effect.

Fixed caustic alkalies precipitate hydrate of the sesquioxide, which dissolves easily and completely in the cold to a green liquid in an excess of the precipitant. After continuous boiling it falls down again completely as anhydrous sesquioxide, leaving the solution colorless.

The sesquioxide of chromium and all its compounds on *fusing with nitre* in presence of an alkali may be easily converted into chromic acid, which combines with the alkali and dissolves in water.

The chromium compounds impart a beautiful *emerald-color* to *borax* $NaO, 2 BO_3$ and *phosphorus salt* * (phos-

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* A laboratory term.

phate of soda and ammonia) NaO, NH_4O, HO, PO_5 in both the flames of the blowpipe.

2. *Insoluble in Potassa.*

[THORINA, YTTRIA, OXIDE OF CERIUM, ZIRCONIA, TITANIC ACID.]

[*a.* THORINA.]
Th O.

This very rare earth, when in the state of freshly precipitated hydrate, is easily soluble in acids, but after having been dried, it dissolves with difficulty, and after being ignited, only in hot sulphuric acid.

Fixed caustic alkalies produce in solutions of thorina a voluminous precipitate, which is quite insoluble in the alkali.

The alkaline carbonates precipitate a basic carbonate of thorina, which dissolves readily in an excess of the precipitant.

An excess of *sulphate of potassa* produces after some time with thorina salts a double compound of sulphate of potassa and thorina, which is quite insoluble in a concentrated solution of the potassa-salt.

[*b.* YTTRIA.]
Y O.

Yttria is soluble in acids, even after ignition; its solutions comport themselves with reagents almost exactly like thorina, it is, however, distinguished from thorina by the double sulphate of yttria and potassa, being soluble in a large quantity of water, and in a dilute solution of sulphate of potassa.

[c. OXIDE AND SESQUIOXIDE OF CERIUM.]

Ce O and Ce$_2$ O$_3$.

This metal is always contained in its saline solutions, after heating with hydrochloric acid, in the form of oxide, since, when sesquioxide is present, it is with evolution of chlorine reduced to oxide. The salts of the oxide, when concentrated, are of an amethyst color.

The caustic alkalies precipitate this oxide as hydrate, which is insoluble in an excess of the precipitant, and becomes yellow on exposure to the atmosphere.

Soluble carbonates precipitate carbonate of oxide, which is slightly soluble in an excess of the precipitant.

Sulphate of potassa throws down after some time a white crystaline double-salt, which is insoluble in an excess of sulphate of potassa.

The oxide is converted into sesquioxide before the blowpipe, and gives with *borax* and *phosphorus salt* a *red* bead in the oxidizing flame, the color of which on cooling disappears partially, but is lost entirely, when exposed to the reducing flame.

[d. ZIRCONIA.]

Zr O.

The natural compounds of zirconia are only completely decomposable by ignition with caustic alkalies. After igniting this earth by itself, it is soluble only in sulphuric acid. It resembles, in its chemical behavior, thorina and yttria more than the other earths; its solutions, however, form, when heated with sulphate of potassa, a white double-salt, which is almost insoluble

in water and acids. It may be distinguished from yttria by its insolubility in acids, after having been ignited.

[e. TITANIC ACID.]
Ti O_2.

The natural compounds of titanic acid are decomposed by fusion with alkaline carbonates, an acid titanate being formed, which is perfectly soluble in cold, or slightly heated, strong hydrochloric acid. Titanic acid is deposited as a white substance from this solution and from solution in acids in general by continuous boiling. After this it is insoluble in all acids, except concentrated sulphuric acid.

It is thrown down from its solution in hydrochloric acid by the *caustic alkalies*, and their *carbonates*, as a white voluminous hydrate of titanic acid, which is insoluble in an excess of alkali, but dissolves completely in cold acids.

It may also be thrown down from its solution in hydrochloric acid (there being no great excess) by *oxalic acid* as an oxalate of titanic acid.

Titanic acid, when precipitated either by boiling or by an alkali, runs through the filter as soon as the acid or the alkali has been washed from it, and renders the filtrate turbid.

If *metallic zinc* (*tin* or *iron*) is brought into a solution of titanic acid in hydrochloric acid, the titanic acid is reduced by the nascent hydrogen to an inferior oxide, which at first dissolves in the acid with a blue color, but by the continued action of the zinc subsides as a violet powder.

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Sulphite of ammonia NH_4O, SO_2 precipitates titanic acid completely from its acid solution by a gentle heat.

Ferrocyanide of potassium $K_2 Cy_3 Fe = K_2 Cfy$ produces in a solution of pure titanic acid a red-brown precipitate, but which is dark-green when the solution contains sesquioxide of iron.

Titanic acid is *not* thrown down by *alkalies* or *sulphide of ammonium* in the presence of *tartaric acid.*

Pure titanic acid gives with *phosphorus salt* after a continued exposure to the inner flame of the blowpipe, a bead, which assumes a *violet-blue* color on cooling; this reaction, which is rendered easier on addition of metallic tin, disappears in the outer flame.

In presence of iron the bead assumes in the inner flame a *blood-red* color.

3. *Soluble as Hydrate in Potassa, but only slightly soluble in acids.*

[TANTALIC ACID.]

$Ta\ O_3.$

The natural compounds of tantalic acid may be decomposed by fusion with *hydrate of potassa*, or *bisulphate of potassa.* Tantalic acid, when ignited by itself, is insoluble in all acids and alkalies; its hydrate, however, dissolves in *potassa*, in *hydrofluoric acid* HF and in *binoxalate of potassa* $KO, \bar{O}, HO, \bar{O}.$ In *sulphuric* and several other acids it is only slightly soluble.

The alkaline carbonates precipitate it again from these solutions; from the solution in sulphuric acid, however, it is thrown down also by water, and in this state, after a continued digestion with strong hydro-

chloric acid, it may be dissolved in considerable quantity. The hydrochloric acid solution becomes turbid on boiling, or on the addition of *sulphuric acid*, or a *sulphate*.

Tantalic acid, precipitated by water from its solution in sulphuric acid, when brought into contact with *zinc* and *dilute hydrochloric acid*, dissolves and forms a fine blue liquid, which after some time becomes dark brown.

II. — METALS WHICH ARE PRECIPITATED BY SULPHIDE OF AMMONIUM AS SULPHIDES.

a. OXIDE OF NICKEL.

Ni O.

The compounds of this oxide with acids are green; its anhydrous salts, or those freed from their water of crystallisation, are pale-yellow.

The solutions of these salts are not thrown down by *hydrosulphuric acid* after acidulation with a strong mineral acid; the neutral compounds of oxide of nickel with mineral acids are only *partially* precipitated by this reagent; but after the addition of a sufficient quantity of an alkaline acetate, they are perfectly thrown down, on heating gently for some time and avoiding the presence of too large a quantity of acetate acid.

Sulphide of ammonium produces in neutral or alkaline solutions of oxide of nickel the same black precipitate; there remains, however, a small quantity of sulphide of nickel dissolved in an excess of this precipitant, which causes the solution after the subsidence of the precipitate to appear brown. Sulphide of nickel is

difficultly soluble in hydrochloric acid, but dissolves readily in nitric acid or nitro-hydrochloric acid.

Ammonia precipitates, even from neutral solutions of these salts, only a small quantity of the hydrate of oxide, which on addition of more ammonia is redissolved, causing the originally green solution to become blue.

Potassa precipitates in this solution, as well as those containing no ammonia, an apple-green hydrate of oxide of nickel.

The alkaline carbonates give a pale-yellow precipitate, which however dissolves easily with a greenish-blue color in an excess of carbonate of ammonia.

The carbonates of the alkaline earths do not precipitate salts of nickel in the cold.

Cyanide of potassium K Cy throws down a greenish-white precipitate of cyanide of nickel Ni Cy, which is readily soluble in an excess of the precipitant, the double-cyanide of nickel and potassium Ni Cy, K Cy being formed. From this solution cyanide of nickel is again thrown down by acids (such as sulphuric or hydrochloric) while the cyanide of potassium is decomposed with evolution of hydrocyanic acid H Cy.

The precipitated cyanide of nickel is soluble in an excess of the acid only at the boiling point. Cyanide of nickel may be precipitated also by free *hydrocyanic acid* from acetate of nickel or from a solution of this metal in mineral acids, to which an alkaline acetate has been added.

In the exterior flame of the blowpipe, nickel-compounds impart to the bead of *borax* or *phosphorus salt* a *reddish* color. When exposed with *borax* to the inner

flame they are reduced to metal, which renders the bead *grey*.

b. OXIDE OF COBALT.
Co O.

Cobalt-salts are generally blue when anhydrous, or in concentrated acid solutions, whilst dilute solutions in water are always of a crimson color.

With *hydrosulphuric acid* and *sulphide of ammonium* cobalt-salts comport themselves like those of oxide of nickel; the precipitate of sulphide of cobalt Co S however is quite insoluble in sulphide of ammonium. They are, like the nickel salts, also precipitated by hydrosulphuric acid in the presence of an alkaline acetate.

From neutral solutions of cobalt, free from ammoni-acal-salts, *ammonia* throws down a part of the oxide as a blue basic salt, which after some time becomes red, but on exposure to the air immediately turns green and then brown; acid solutions or solutions containing ammoniacal salts yield with ammonia a clear red liquid, which quickly absorbs oxygen from the air and deposits the brown hydrate of the sesquioxide.

Cobalt-solutions free from atmospheric air give with the *fixed caustic alkalies* a flocculent blue precipitate, which on boiling takes a rose color, and by exposure to the atmosphere becomes olive-green or dirty-violet, with absorption of oxygen. Salts of cobalt containing much ammoniacal salts, excluded from the atmosphere, give no precipitate with potassa, but with access of the air a slight brown precipitate.

The alkaline carbonates precipitate a pink carbonate

of the oxide, which dissolves with the same color in an excess of carbonate of ammonia.

The carbonates of the alkaline earths give no precipitate in the cold.

Cyanide of potassium precipitates from acid solutions of cobalt-salts a brownish-white cyanide of cobalt, $Co\ Cy$, dissolving easily in an excess of the precipitant, from which solution the cyanide of cobalt cannot be again precipitated by acids, as it exists now in the form of cobalticyanide of potassium, $K_3\ Co_2\ Co_6$.

$$2\ Co\ Cy + 3\ K\ Cy + H\ Cy = K_3\ Co_2\ Cy_6 + H.$$

If the salt of cobalt contains nickel, the addition of hydrochloric acid to the solution of the cyanides produces a greenish precipitate, which always contains the whole of the nickel, and under particular circumstances all the cobalt, that is, when these two metals are in the proportion of 3 equivalents of nickel to 2 equivalents of cobalt. The precipitate consists then of cobalticyanide of nickel, $Ni_3\ Co_2\ Cy_6$. In case of a larger proportion of nickel the precipitated cyanide of nickel is mixed with the former compound; but if the proportion of nickel is smaller, a part of the cobalt remains in solution as cobalticyanide of potassium.

Borax and *phosphorus salt* give with salts of cobalt in both the flames of the blowpipe a beautiful *blue* glass, the color of which is scarcely affected by the presence of other oxides of this group.

c. OXIDE OF MANGANESE.
Mn O.

Most of the salts of this oxide dissolve in water, yielding pale rose-colored solutions, and all of them are

soluble in hydrochloric acid; this oxide is formed with evolution of chlorine, when the higher oxides of manganese are acted on by hydrochloric acid, and heated.

No precipitate is produced by *hydrosulphuric acid* in solutions of the salts of the oxide of manganese, not even in the acetate.

Sulphide of ammonium precipitates the metal completely in the form of a bright flesh-colored sulphide, which is readily soluble in strong acetic acid, and which, by absorption of oxygen from the air, assumes a brownish-black color.

The fixed caustic alkalies precipitate this metal as a white hydrate of the oxide, which soon becomes brown on exposure to the air.

Ammonia throws down from the neutral salts only the half of this oxide as a white hydrate, which, in contact with the air, becomes brown. This hydrate is soluble in chloride of ammonium, and therefore no precipitate is produced by ammonia in a solution containing free hydrochloric acid. A solution of a salt of oxide of manganese, however, containing free ammonia, becomes turbid on exposure to the air, and deposits after a time all the metal in the form of brown hydrate of the sesquioxide, provided there is a sufficient quantity of ammonia present.

Alkaline carbonates precipitate white carbonate of the oxide of manganese, which is very slightly soluble in chloride of ammonium, and becomes brown on exposure to the air.

The carbonates of the alkaline earths do not decompose the salts of the oxide of manganese in the cold.

By fusing a compound of manganese with *carbonate*

of soda, upon platinum foil, the *green* manganate of soda is produced. This is one of the most delicate tests for manganese. The addition of a small quantity of an oxidising substance, such as *nitrate* or *chlorate of potassa*, renders the reaction still more certain.

With *borax* and *phosphorus salt*, the compounds of manganese produce in the oxidising flame of the blow-pipe an *amethyst-colored* bead, the color of which disappears in the reducing flame.

d. OXIDE OF IRON.

Fe O.

The salts of this oxide, in dilute solution, are colorless, but possess a pale greenish-blue color in concentrated; when anhydrous, they are white. They absorb oxygen from the air, the oxide passing into sesquioxide, which, from neutral solutions, is deposited as a yellow basic salt. This conversion is effected more quickly and completely by oxidising agents, such as *chlorine*, *hypochlorus acid*, or boiling with *nitric acid*. In oxidising with nitric acid in the first stage of the process, a peculiar compound of binoxide of nitrogen with the remainder of the oxide of iron is formed, imparting a greenish-brown color to the solution. The application of heat destroys this compound with disengagement of binoxide of nitrogen. (Test for nitric acid.)

Hydrosulphuric acid forms only a very slight precipitate of black sulphide of iron, Fe S, in solutions of neutral compounds of the oxide with strong mineral acids; in acid solutions no precipitate whatever is produced with the exception of the acetate (or a mixture

of a salt of the oxide with an alkaline acetate) which is partially precipitated.

Sulphide of ammonium throws down iron completely as a black sulphide, which is insoluble in an excess of the precipitant; but when tartaric acid or any other non-volatile organic acid is present, a small quantity of the sulphide remains suspended in the liquid, imparting to it a light-green color ; this is deposited however on heating, and the liquid assumes a bright-yellow color (from excess of sulphide of ammonum). Sulphide of iron on exposure to the air is very rapidly converted into brown sesquioxide.

Fixed caustic alkalies precipitate from salts of the oxide of iron a white hydrate of the oxide, which, on exposure to the air, immediately becomes of a dingy green, and at last a reddish-brown color.

Ammonia precipitates the salts of the oxide of iron only *partially*, and not at all when the solution contains a sufficient quantity of free acid or ammoniacal salts ; the solution, however, containing free ammonia absorbs oxygen from the air, and deposits a dingy green precipitate, which gradually passes into red sesquioxide of iron.

Alkaline carbonates precipitate white carbonate of the oxide, which is soluble in chloride of ammonium, and comports itself like the pure oxide.

Carbonates of the alkaline earths produce no precipitate.

Ferrocyanide of potassium forms with solutions of the salts of oxide of iron (absolutely free from sesquioxide and atmospheric air) a white precipitate of ferrocyanide of iron and potassium, $K Fe_3 Cfy_2$. This

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precipitate assumes a bluish tint when small quantities of air or sesquioxide of iron are present, and passes instantaneously into Prussian blue, 4 Fe 3 Cfy, by the action of chlorine or nitric acid. The transformation is represented by the following equation:—

$$3 \text{ K Fe}_3 \text{ Cfy}_2 + 4 \text{ O} = 2 \text{ Fe}_4 \text{ Cfy}_3 + 3 \text{ KO} + \text{Fe O}.$$
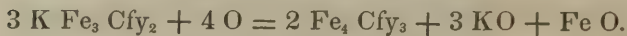
The oxide of iron separated by the oxygen of the air is soon converted into sesquioxide. When chlorine or nitric acid is employed, chlorides or nitrates of iron and potassium are formed.

Ferricyanide of potassium, $K_3 \text{ Cfy}_2$, produces with salts of oxide of iron immediately a beautiful blue precipitate of ferricyanide of iron, $\text{Fe}_3 \text{ Cfy}_2$, in which the three equivalents of potassium in the potassium salt are replaced by three equivalents of iron.

These two precipitates are insoluble in acids, but may be easily decomposed by alkalies with separation of the oxide of iron, and reproduction of an alkaline ferrocyanide or ferricyanide.

Before the blowpipe, the compounds of oxide of iron exhibit the same character as those of sesquioxide (*v.* p. 28).

e. SESQUIOXIDE OF IRON.

$\text{Fe}_2 \text{ O}_3.$

Almost all the salts of the sesquioxide form with water, or when they are not soluble in water, with hydrochloric acid, brownish-yellow solutions.

Neutral solutions of sesquioxide of iron, or acid solutions in the presence of an alkaline acetate, are decom-

posed by boiling with the separation of hydrate of the sesquioxide.

Metallic iron, sulphurous acid or *hydrosulphuric acid* reduce the salts of the sesquioxide to salts of the oxide, the last with deposition of sulphur, which renders the liquid milky.

$$Fe_2O_3, \ 3\,SO_3 + Fe = 3\,(FeO, \ SO_3)$$
$$Fe_2O_3, \ 3\,SO_3 + SO_2 = 2\,(FeO, \ SO_3) + 2\,SO_3$$
$$Fe_2O_3, \ 3\,SO_3 + HS = 2\,(FeO, \ SO_3) + HO, \ SO_3 + S.$$
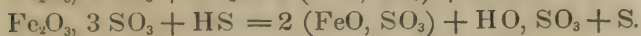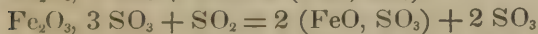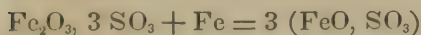
The behavior of salts of the sesquioxide of iron with *sulphide of ammonium* is the same as that of salts of the oxide, the precipitate containing, however, free sulphur in admixture.

Potassa, soda and *ammonia* throw down from salts of the sesquioxide of iron hydrate of sesquioxide, $2\,HO, \ Fe_2O_3$, which is insoluble in the precipitants and in ammoniacal salts; the presence, however, of fixed organic acids, sugar, etc. prevents this precipitation.

Alkaline carbonates produce the same precipitate with evolution of carbonic acid.

The salts of sesquioxide of iron are thrown down completely by the *carbonates of the alkaline earths* even in the cold.

Phosphate of soda precipitates the white phosphate of iron, $2\,Fe_2O, \ 3\,PO_5 + 13$ aq., which becomes brown by the action of free alkalies, and dissolves in ammonia, a great excess of phosphate of soda being present. Phosphate of sesquioxide of iron is insoluble in acetic acid. (Separation of iron from the phosphates of the alkaline earths.)

Ferrocyanide of potassium forms a beautiful blue

precipitate of ferrocyanide of iron (Prussian blue, Fe_4 Cfy_3) which is insoluble in hydrochloric acid.

$$3 K_2 Cfy + 2 (Fe_2 O_3, 3 SO_3) = Fe_4 Cfy_3 + 6 (KO, SO_3).$$
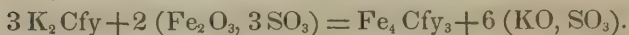
Ferricyanide of potassium produces no precipitate, but it imparts a darker color to the liquid.

With *borax* and *phosphorus salt* all the compounds of iron produce in the outer blowpipe-flame *dark-red* beads, which become lighter on cooling. On exposure to the inner blowpipe-flame, these beads assume a *bottle-green* color, which on cooling disappears entirely.

From the other members of this group iron is always separated in the form of sesquioxide. For this purpose the solution of the precipitate produced by sulphide of ammonium in hydrochloric acid, when by its black or grey color the presence of iron is indicated, is boiled with the addition of a few drops of nitric acid.

f. OXIDE OF ZINC.

Zn O.

Most salts of this oxide are soluble in water, and all of them in hydrochloric acid.

From salts containing weak acids, such as acetic acid, or from salts with mineral acids in the presence of an alkaline acetate, oxide of zinc is completely thrown down by *hydrosulphuric acid* in the form of white sulphide of zinc, $Zn S$, which is insoluble in potassa; but if the solution contains a *sufficient* quantity of free mineral acid, *hydrosulphuric acid* produces no precipitate.

Sulphide of ammonium precipitates the zinc-salts completely as sulphides.

Caustic alkalies throw down this oxide in the form of a white hydrate, HO, ZnO, which is easily soluble in an excess of the precipitant.

The *carbonates of the fixed alkalies* produce a basic carbonate of zinc, 3 (H O, ZnO), 2 (ZnO, C O$_2$), insoluble in the precipitant, but soluble in chloride of ammonium, the presence of which, therefore, prevents its formation.

Carbonate of ammonia precipitates carbonate of zinc, which is readily dissolved in an excess of the precipitant.

The carbonates of the alkaline earths produce no precipitate with zinc-salts.

The compounds of zinc, when exposed with *carbonate of soda* upon charcoal to the inner flame of the blowpipe, produce a white incrustation of oxide of zinc. When moistened with a solution of cobalt and strongly heated, they assume a *green* color.

[*g.* SESQUIOXIDE OF URANIUM.]

Ur$_2$ O$_3$.

The salts of this sesquioxide are soluble in water or hydrochloric acid, forming a yellow-colored solution.

Hydrosulphuric acid reduces them to salts of the oxide which are easily reconverted into salts of sesquioxide by exposure to the atmosphere, or by the action of nitric acid even in the cold.

Sulphide of ammonium precipitates from salts of both the oxides of uranium, black sulphides of uranium, Ur S and Ur$_2$ S$_3$, which in the first case is only

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slowly deposited, the solution remaining black for some time.

Caustic alkalies precipitate a pale-yellow compound of the sesquioxide with the alkali, which is insoluble in the precipitant.

Alkaline carbonates produce a pale-yellow precipitate, which is soluble in an excess of carbonate of ammonia, but is deposited again from this solution by boiling.

Salts of sesquioxide of uranium, like the corresponding salts of iron, are precipitated by the *carbonates of the alkaline earths*.

A boiling solution of *sulphite of ammonia* precipitates yellow sulphite of sesquioxide of uranium.

Ferrocyanide of potassium produces a fine red-brown precipitate.

The salts of the oxide of uranium exhibit exactly the same reaction as those of the sesquioxide; their solutions and the compounds precipitated from them by the *caustic* and *carbonated alkalies* are for the most part *green*, with a grey or brownish tint, when mixed with sesquioxide.

The compounds of uranium in the outer flame of the blowpipe impart to *phosphorus-salt* a *yellowish-green* color, to borax a pure *yellow* color, both of which become *green* when heated in the *inner flame.*

Some of the oxides of this group, namely, the oxides of cobalt, iron, manganese, and zinc, form double compounds with ammoniacal salts (chloride of ammonium), which are not decomposed and precipitated by the alkalies. The oxide of nikel, however, is thrown down in the presence of ammoniacal salts

by the *fixed alkalies.* Sesquioxide of iron and uranium under the same circumstances may be completely precipitated even by *ammonia;* but this is prevented by the presence of non-volatile organic acids.

With phosphoric acid all the members of this group form compounds insoluble in water, but soluble in mineral acids, and, with the exception of oxide of zinc, they are all insoluble in the fixed alkalies.

GROUP IV.

METALS, THE SULPHIDES OF WHICH ARE INSOLUBLE IN DILUTE MINERAL ACIDS, AND WHICH MAY THEREFORE BE PRECIPITATED FROM THEIR ACID SOLUTION BY HYDROSULPHURIC ACID.

This group of metals is divided into two sections, distinguished by the nature of their oxygen-, and sulphur-compounds.

A. Metals, the oxygen- and sulphur-compounds of which possess the properties of bases.

Lead, silver, mercury, bismuth, copper, cadmium, [palladium, rhodium, and osmium.]

The sulphides of these metals do not dissolve in the soluble sulpho-bases (sulphide of potassium, sulphide of ammonium.)

B. Metals, the oxygen- and sulphur-compounds of which possess the properties of acids.

Antimony, arsenic, tin, gold, platinum, [iridium, selenium, tellurium, tungsten, molybdenum, and vanadium.]

The sulphides of these metals dissolve in the soluble sulpho-bases, and form sulpho-salts, corresponding with their oxygen-salts, such as —

Antimoniate of potassa, . . . KO, SbO_5

Sulphantimoniate of sulphide of potassium . KS, SbS_5

Stannate of potassa . . . KO, SnO

Sulphostannate of sulphide of potassium . KS, SnS_2

Tungstate of potassa . . . KO, WO_3

Sulphotungstate of sulphide of potassium . KS, WS_3

When a solution of these sulpho-salts (in analysis we generally obtain solutions of one of the latter class of sulphides in sulphide of ammonium) is treated with a free acid, the sulpho-acid is thrown down with its peculiar color, with evolution of hydrosulphuric acid; the product of decomposition of the sulpho-base.

$$3\,KS, SbS_5 + 3\,H\,Cl = Sb\,S_5 + 3\,K\,Cl + 3\,HS.$$

On treating a precipitate consisting of several sulphides of these two divisions, as, for instance, sulphide of silver and sulphide of arsenic, with sulphide of ammonium at a gentle heat, the acid sulphide (sulphide of arsenic) dissolves, whilst the basic sulphide (sulphide of silver) remains insoluble; in this manner these two metals may be completely separated by filtering and washing. From this solution in sulphide of ammonium, sulphide of arsenic is then precipitated by hydrochloric acid and examined by the peculiar reagents.

I. — BEHAVIOR OF THE OXIDES OF THE FIRST DIVISION OF THIS GROUP.

a. OXIDE OF LEAD.

Pb O.

The salts of this oxide are colorless, if the acid in combination is colorless.

Solutions of these salts are thrown down by *hydrosulphuric acid* and *sulphide of ammonium* as black sulphide of lead, Pb S; even its insoluble compounds, on digestion with sulphide of ammonium, are converted into sulphide of lead. In presence of much hydrochloric acid the precipitate is brown or sometimes red.

Hydrochloric acid or *soluble chlorides* precipitate from moderately dilute solutions of this oxide, the white chloride of lead Pb Cl, which is soluble in potassa, and also in a large proportion of water.

Sulphuric acid and *soluble sulphates* throw down white sulphate of lead, Pb O, SO$_3$.

Solutions of oxide of lead give, with *chromates*, a yellow precipitate of chromate of lead: with *arseniates*, *phosphates*, and *oxalates*, the corresponding salts of lead, all of which are white. Of these precipitates, the sulphate and chromate are insoluble in dilute nitric acid, while the others are slightly soluble in the same; all, however, dissolve in the fixed caustic alkalies.

Ammonia throws down from salts of lead, with the exception of the acetate, the white hydrate of the oxide, which is insoluble in an excess of the precipitant.

Fixed caustic alkalies produce the same precipitate, which is however soluble in a great excess of the alkali.

The *alkaline carbonates* precipitate carbonate of lead, insoluble in an excess of the precipitant, but soluble in caustic potassa.

All compounds of lead, on heating before the blow-pipe with a reducing agent (such as *carbonate of soda* or *cyanide of potassium*), yield a malleable metallic globule and a yellow incrustation of oxide.

b. OXIDE OF SILVER.

Ag O.

Almost all the silver-salts are colorless, and with a few exceptions leave, after ignition, metallic silver.

They are decomposed with precipitation of silver by many *metals*, as *zinc, iron, copper*, etc.; also, by *sulphate of oxide of iron, chloride of tin, sulphurous acid*, and various *organic compounds*.

Hydrosulphuric acid and *sulphide of ammonium* precipitate black sulphide of silver, Ag S.

Hydrochloric acid or *soluble chlorides* throw down white curdy chloride of silver, Ag Cl, easily soluble in ammonia, insoluble in nitric acid.

Fixed caustic alkalies give a brown precipitate of oxide of silver.

Ammonia does not give any precipitate with acid silver solutions; neutral solutions it renders slightly turbid.

The *alkaline carbonates* precipitate white carbonate of silver, which is soluble in an excess of carbonate of ammonia.

c. SUBOXIDE OF MERCURY.

$$Hg_2 O.$$

The neutral salts of suboxide of mercury are white; the basic salts are yellow.

Some of the neutral salts are decomposed by water with separation of basic salts. The subsalts of mercury are reduced by many metals, such as *zinc, iron, copper,* etc.; also, by *sulphate of oxide of iron, chloride of tin, sulphurous acid,* and various *organic compounds.*

Hydrosulphuric acid and *sulphide of ammonium* precipitate black subsulphide, $Hg_2 S$, which is insoluble in sulphide of ammonium. *Potassa* decomposes it, forming sulphide of mercury and separating metallic mercury.

Hydrochloric acid and *soluble chlorides* throw down from these salts white subchloride of mercury, $Hg_2 Cl$, which the *caustic alkalies* convert into black suboxide.

The same precipitate, $Hg_2 O$, is obtained by means of *caustic alkalies* from solutions of subsalts of mercury.

The *alkaline carbonates* produce a precipitate of carbonate of suboxide of mercury.

Oxide of lead, oxide of silver, and suboxide of mercury, are the only oxides of this group which may be precipitated from their solution partially (lead) or completely by *hydrochloric acid.* Chloride of lead is easily recognised by being soluble in water, chloride of silver by being soluble in ammonia, and separated from this solution by nitric acid; subchloride of mercury by being blackened by ammonia.

d. OXIDE OF MERCURY.

Hg O.

In regard to color and behavior with water the salts of the oxide of mercury resemble very much the salts of suboxide. They are reduced to the metallic state by the same substances, passing generally at first into suboxide.

Hydrosulphuric acid and *sulphide of ammonium* precipitate black sulphide of mercury, Hg S, which is soluble in caustic potassa, only when much sulphide of ammonium is present. On the addition of a small quantity of hydrosulphuric acid, or sulphide of ammonium, the precipitate is white, being a compound of sulphide of mercury with the undecomposed mercurysalt, ex. g. $2 \, HgS + HgCl$. On adding more hydrosulphuric acid this compound is decomposed, and all the mercury is thrown down as black sulphide. This is the only sulphide of this group which is insoluble in boiling concentrated nitric acid; it dissolves, however, easily in nitro-hydrochloric acid.

Ammonia and *carbonate of ammonia* give a white precipitate with salts of oxide of mercury, which is a compound of amidide of mercury with undecomposed mercury-salts, ex. g. $2 \, HgCl + NH_3 = (HgNH_2, \, HgCl) + HCl$.

The fixed alkalies throw down a yellow hydrate of the oxide, HO, HgO, but when ammoniacal salts are present, the ammonia which is set free precipitates the above-mentioned amidogen double compounds.

The carbonates of the fixed alkalies produce a similar effect.

All compounds of mercury, when heated in a glass tube (closed at one end) with an alkaline carbonate, are decomposed with separation of small globules of metallic mercury, which may be easily recognised with the assistance of a small lens. The experiment succeeds best when the carbonate is previously slightly moistened.

Mercury, when in neutral or slightly acid solution, may also be detected by reduction to the metallic state by means of another metal. Strips of perfectly bright *copper-foil* are selected for this purpose, upon which, after a short time, the mercury is deposited as a grey coating, which, on being rubbed, assumes a metallic lustre and disappears when heated.

e. TEROXIDE OF BISMUTH.

$Bi O_3$.

Most compounds of this oxide are colorless; all are soluble in dilute mineral acids. These solutions, unless a very great quantity of acid be present, are decomposed by much water with the formation of an acid compound, which is soluble, and a basic compound, which is nearly insoluble. Terchloride of bismuth most strikingly exhibits this behavior, for which reason the nitric acid solution of the oxide to be examined is evaporated with a slight addition of hydrochloric acid, in order to convert the nitrate into chloride. If now, the solution, not quite evaporated to dryness, is poured into a large quantity of water, the presence of bismuth causes a precipitate of basic chloride of bismuth.

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$$3 \text{ Bi Cl}_3 + 6 \text{ H O} = \text{Bi Cl}_3, 2 \text{ Bi O}_3 + 6 \text{ H Cl.}$$
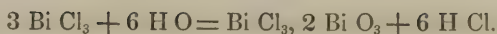
The free acid, however, still retains a small quantity of teroxide in solution.

Hydrosulphuric acid and *sulphide of ammonium* throw down the brownish-black tritosulphide of bismuth, Bi S_3.

The alkalies precipitate a white hydrate insoluble in excess.

The alkaline carbonates give a precipitate of carbonate of bismuth slightly soluble in an excess of the carbonate.

Chromate of potassa throws down yellow chromate of bismuth, soluble in nitric acid, but insoluble in caustic potassa.

Compounds of bismuth, when heated upon charcoal in the inner flame of the blowpipe, with reducing agents, yield a brittle metallic globule and a yellow incrustation.

f. OXIDE OF COPPER.

Cu O.

The salts of this oxide, when anhydrous, are white; when in the state of hydrate in solution most of them are blue. Chloride of copper is emerald-green.

By several *metals*, especially by *iron*, copper may be thrown down from its solutions in the metallic state. A bright iron rod becomes covered with a copper-red coating, even when a very small quantity of copper is present, provided the solution be neutral or only very slightly acid.

Hydrosulphuric acid or *sulphide of ammonium* pre-

cipitates black sulphide of copper, which is only slightly soluble in the latter.

Fixed caustic alkalies throw down in the cold, blue hydrate of oxide of copper, HO, Cu O, which, on boiling, loses the water and becomes black.

Ammonia precipitates at first a green basic salt or blue hydrate of the oxide, which dissolves in excess of ammonia with a beautiful azure-blue color. In the presence of very small quantities of copper, this color is only perceived by looking through a considerable body of the fluid.

Carbonate of ammonia acts with copper-salts like caustic ammonia.

The carbonates of the fixed alkalies throw down a greenish-blue basic carbonate of copper, which, by boiling with an excess of alkali, is converted into black oxide of copper.

Cyanide of potassium precipitates a yellowish-green cyanide of copper, Cu Cy, soluble in excess of cyanide of potassium.

Ferrocyanide of potassium produces even in very dilute solutions a dark purple-red precipitate of ferrocyanide of copper, Cu_2 Cfy.

By boiling with *alkaline sulphites*, with *salts of oxide of iron*, and with many *organic substances* (such as *sugar*), salts of oxide of copper, especially when free alkali is present, are easily reduced to suboxide.

Salts of copper, when heated in the oxidising flame of the blowpipe, impart to *borax* and *phosphorus-salt* a beautiful *green* color, becoming *blue* on cooling; in the reducing flame (especially on addition of some tin) these beads become colorless, assuming generally on cooling a *dirty brown-red* color.

Compounds of copper, when heated upon charcoal with reducing agents, yield metallic copper, by which process even mere traces of this metal may be detected with certainty.

g. OXIDE OF CADMIUM.
Cd O.

The compounds of oxide of cadmium are white, and soluble in water or hydrochloric acid.

Hydrosulphuric acid and *sulphide of ammonium* produce, even in strongly acid solutions, an orange-yellow precipitate of sulphide of cadmium, Cd S, which is insoluble in sulphide of ammonium as well as the alkalies.

Ammonia throws down the white hydrate of this oxide, HO, CdO, easily soluble in an excess of ammonia; from this solution sulphide of cadmium is thrown down by hydrosulphuric acid.

The fixed caustic alkalies produce the same precipitate as ammonia, but do not redissolve it when in excess.

The alkaline carbonates throw down carbonate of cadmium, insoluble in excess of the precipitant.

Compounds of cadmium, when exposed upon charcoal to the inner flame of the blowpipe, yield with reducing agents a *yellow* or *reddish-brown* incrustation of oxide of cadmium.

[*h*. OXIDE OF PALLADIUM.]
Pd O.

Palladium dissolves in nitric acid, or nitro-hydrochloric acid, with a red-brown color.

These solutions contain a salt of the oxide.

The anhydrous salts, when ignited by themselves, yield metallic palladium. They are reduced to the metallic state also by the action of *sulphurous acid* (*sulphites*), and by all the metals which precipitate silver in the metallic state. The same effect is produced by the addition of a *salt of oxide of iron* or *a formiate* being gently heated.

Hydrosulphuric acid and *sulphide of ammonium* precipitate a dark-brown sulphide of palladium, PdS, insoluble in sulphide of ammonium.

Hydriodic acid, HI, and *iodide of potassium*, KI, precipitate black iodide of palladium, PdI, which, however, is not formed immediately in very dilute solutions.

Cyanide of potassium and *cyanide of mercury*, Hg Cy, yield a yellowish-white gelatinous precipitate of cyanide of palladium, Pd Cy, which is soluble in a large quantity of hydrochloric acid.

Ammonia added to nitrate of palladium produces only a discoloration, but no precipitate, whilst with chloride of palladium it precipitates a compound of chloride of palladium and ammonia, Pd Cl, NH$_3$, which dissolves again in an excess of ammonia.

The fixed caustic alkalies and *their carbonates* precipitate a yellowish-brown basic salt, soluble in an excess of the precipitant.

Carbonate of ammonia produces the same effect.

[*i.* SESQUIOXIDE OF RHODIUM.]
R$_2$ O$_3$.

Rhodium and anhydrous sesquioxide of rhodium are

4 *

insoluble in all acids. This metal, however, when alloyed with either platinum, copper, lead, or bismuth, dissolves in nitro-hydrochloric acid. Both the metal and its oxide dissolve on fusion with *bisulphate of potassa*, or on heating a mixture of both with *chloride of sodium* to redness, and passing a stream of *chlorine* over it.

The solutions of sesquioxide of rhodium are generally of a beautiful rose-red color; the solution obtained by fusion with bisulphate of potassa is yellow, but becomes red on digestion with hydrochloric acid.

Hydrosulphuric acid throws down from the salts of rhodium a brown sesquisulphide, $R_2 S_3$. This precipitate appears only after a short time, and the supernatant liquid remains red for some time.

Sulphide of ammonium acts like hydrosulphuric acid. Sulphide of rhodium is insoluble in an excess of sulphide of ammonium.

Ammonia and *carbonate of ammonia* throw down after some time a yellow double compound of sesquioxide of rhodium and ammonia, which is soluble in hydrochloric acid.

The fixed caustic alkalies and their carbonates give after long boiling a yellowish-brown precipitate.

The red color of the solutions of this sesquioxide (which after treatment with hydrosulphuric acid is still visible) and its insolubility in acids distinguish rhodium from all other metals.

[*k.* OXIDES OF OSMIUM.]

Os O, Os O_4.
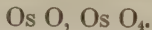
Metallic osmium, especially in the state of fine pow-

der, when ignited in atmospheric air or oxygen, is converted into osmic acid, $Os\,O_4$, the vapor of which resembles chlorine and iodine, but is even more insupportable.

The inferior oxides, when ignited in contact with air, are also converted into osmic acid.

Osmium dissolves in nitric and nitro-hydrochloric acid, osmic acid volatilising, which may be easily recognised by its suffocating smell.

Solutions of the salts of oxide of osmium and of osmic acid in water, acids and alkalies, are precipitated by *hydrosulphuric acid* as a brownish-black sulphide, which is insoluble in *sulphide of ammonium*.

Osmic acid in solution is reduced to the metallic state by most of the metals, even by *mercury*, by *sulphate of oxide of iron*, by the *sulphites*, which render the liquid blue, and by many *organic compounds*, such as *alcohol, ether, fats, formic acid,* etc.

When metallic osmium, or a platinum ore containing osmium, is heated upon the edge of a piece of platinum foil in a spirit flame, the osmic acid, which is formed, is immediately again reduced to metal and greatly increases the illuminating power of the flame.

Osmium, rhodium, and palladium, are very rare metals; they are but seldom found except in ores of platinum, and then in company with iridium; it is therefore seldom necessary to search for these metals, except in the residue of platinum ores. In the state of pure salts they are easily recognised by the tests above mentioned.

BEHAVIOR OF THE METALS OF THE SECOND DIVISION.

The comportment of these metals and their compounds with acids, the color of their sulphides, etc., enable us to divide them into the following subdivisions.

1. *SUBDIVISION.*

ANTIMONY, TIN, ARSENIC.

These three metals are soluble in nitro-hydrochloric acid. Antimony and tin are converted by strong nitric acid into white oxides, which are insoluble in an excess of the acid; arsenic dissolves in nitric acid in the form of arsenic acid. The solutions of their sulphides in sulphide of ammonium are thrown down by free acids, antimony as an orange red, tin and arsenic as yellow precipitates.

2. *SUBDIVISION.*

PLATINUM, [IRIDIUM,] GOLD.

These metals are soluble only in nitro-hydrochloric acid, and not at all affected by nitric acid. The solutions of their sulphides in sulphide of ammonium are thrown down by free acids as black or brownish precipitates. All their compounds, when ignited, yield pure metal, as a porous mass (sponge), or a bright powder.

3. *SUBDIVISION.*

[SELENIUM, TELLURIUM.]

These two bodies are volatile, and exhibit a peculiar smell when exposed to the air, somewhat resembling

that of arsenic.   They are easily soluble in nitric acid ; this solution contains selenious and tellurous acids, which, on being heated with *sulphurous acid*, are reduced to selenium (red) and tellurium (black).

With *hydrosulphuric acid* insoluble precipitates are produced of sulphide of selenium (reddish-yellow), and sulphide of tellurium (black).

4. *SUBDIVISION.*

[TUNGSTEN, VANADIUM, MOLYBDENUM.]

The higher oxides of these three metals are easily reduced to lower ones, remaining in solution, generally with a fine blue color, by reducing agents, tungstic and molybdic acid by metallic *zinc*, vanadic acid by *hydrosulphuric acid.*

1. *SUBDIVISION.*

a. OXIDES OF ANTIMONY.

[TEROXIDE OF ANTIMONY.]

Sb O_3.

Metallic antimony is volatile, but only at an intense red heat, and in a current of air or gas before the blowpipe, it may easily be fused into a globule with a bright metallic surface, which by continued blowing is completely volatilised with disengagement of white inodorous fumes of teroxide of antimony.

The globule is brittle, and may be powdered.

By the action of *nitric acid* upon antimony, according to the concentration of the acid, teroxide of antimony, or antimonic acid, or a mixture of both, is formed,

insoluble in an excess of nitric acid, but soluble in tar-
taric acid.   On fusing antimony or a compound of
antimony with *nitre*, antimonic acid is formed ; in the
case of sulphur being present in this compound, sul-
phuric acid at the same time is produced.

Antimony is readily dissolved in nitro-hydrochloric
acid; this solution contains quinquichloride of antimony,
$Sb\ Cl_5$.

Tersulphide of antimony is dissolved in strong hydro-
chloric acid with disengagement of hydrosulphuric acid.
The solution contains the terchloride, $Sb\ Cl_3$.

The compounds of teroxide of antimony with acids
are decomposed by the addition of a large quantity of
water, a white basic salt being separated, ex. gr.

$$6\ Sb\ Cl_3 + 15\ H\ O = 15\ H\ Cl + Sb\ Cl_3,\ 5\ Sb\ O_3.$$
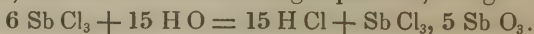
The liberated acid however contains always a cer-
tain quantity of teroxide in solution.   Tartaric acid
readily dissolves this basic compound, or prevents its
formation; this constitutes a distinction between the
salts of antimony and bismuth.

Hydrosulphuric acid separates the antimony com-
pletely from the acid solutions of the teroxide in the
form of tersulphide, $Sb\ S_3$, which is readily soluble in
potassa and sulphide of ammonium, very little soluble
in ammonia, and insoluble in bicarbonate of ammonia.

Ammonia and *carbonate of ammonia* (the latter with
disengagement of carbonic acid) throw down teroxide
of antimony completely; the precipitate is insoluble in
an excess of the precipitant.

The *fixed caustic alkalies* likewise precipitate ter-
oxide, which dissolves however in an excess of the
alkali.

This deportment is modified to a certain extent by the presence of tartaric acid. The solution of the double tartrate of antimony and potassa (tartar emetic) is not precipitated by the *alkalies* and their *carbonates*, or only after the lapse of some time; in presence however of a mineral acid, *hydrosulphuric acid* separates from this solution all the metal. In the solution of this double tartrate, *hydrochloric, nitric,* and *sulphuric acids* produce white precipitates, which are soluble in an excess of hydrochloric.

Metallic zinc precipitates from salts of teroxide of antimony the metal as a black powder, and in the presence of nitric acid also teroxide.

If a salt of teroxide of antimony meet with *sulphuric acid* and *zinc*, antimony unites with the nascent hydrogen and terhydride of antimony (antimonietted hydrogen), $Sb\,H_3$, is disengaged, which is an inodorous gas, and burns in contact with the atmosphere with the formation of water and teroxide of antimony. On depressing a cold porcelain surface upon the flame of this gas metallic antimony is deposited as a black spot without lustre.

A similar reaction is produced on passing terhydride of antimony through a glass-tube and heating the middle of the tube by a spirit lamp; in this experiment a shining metallic mirror is obtained, which is converted into sulphide of antimony on being gently heated in an atmosphere of dry *hydrosulphuric acid.*

Sulphides of antimony may be easily distinguished from similar compounds by dry *hydrochloric acid*, hydrosulphuric acid, and volatile chlorides of antimony being produced.

ANTIMONIC ACID.

$Sb\,O_5$.

Antimonic acid forms insoluble or slightly soluble salts with almost all bases. When freshly precipitated this acid dissolves best in potassa.

On fusing antimonic acid with an excess of *alkali* (or what is the same, metallic antimony or tersulphide of antimony, with *nitre* and an *alkaline carbonate*) a white mass is obtained, from which water dissolves a small quantity of a basic antimoniate of potassa, leaving an insoluble residue behind, which is an acid salt.

Acids, especially *nitric acid*, precipitate the antimonic acid completely from the alkaline solution.

Hydrosulphuric acid throws down from acid solutions of antimonic acid, orange-yellow quinquisulphide of antimony, $Sb\,S_5$. Alkaline solutions are not precipitated by this reagent.

All compounds of antimony, when exposed with *cyanide of potassium*, or *carbonate of soda*, to the reducing flame of the blowpipe, yield globules of the brittle metal, a quantity of which being burned and volatilised, forms a white incrustation of the teroxide on the charcoal.

b. OXIDES OF TIN.

OXIDE OF TIN.

$Sn\,O$.

Metallic tin dissolves in hot hydrochloric acid with disengagement of hydrogen, a chloride, $Sn\,Cl$, being formed, which corresponds to the oxide; the solution

of tin in nitro-hydrochloric acid contains the bichloride, $Sn\ Cl_2$, corresponding to the binoxide. Nitric acid converts metallic tin into hydrate of the binoxide, which is insoluble in the acid.

Salts of oxide of tin, when exposed to the atmosphere, pass by absorption of oxygen into salts of the binoxide.

Hydrosulphuric acid and *sulphide of ammonium* produce in salts of oxide of tin a dark-brown precipitate of sulphide of tin, $Sn\ S$, soluble in a large excess of sulphide of ammonium, if this reagent contains a sufficient amount of sulphur to convert the sulphide into the bisulphide $Sn\ S_2$. Acids precipitate from this solution yellow bisulphide.

Ammonia and *carbonate of ammonia* throw down a white hydrate of the oxide of tin, which is insoluble in an excess of the precipitant.

The fixed caustic alkalies and their *carbonates* precipitate the same hydrate, which dissolves in an excess of the alkali (but not in the alkaline carbonate), from which solution half the quantity of tin is separated by heat in the form of a black powder, binoxide of tin remaining in solution.

$$2\ Sn\ O + 2\ K O = Sn + 2\ K O + Sn\ O_2.$$
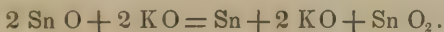
Salts of oxide of tin, by their tendency to absorb oxygen, are powerful reducing agents (in general the chloride is employed); salts of *sesquioxide of iron* and of *oxide copper* are respectively converted into salts of the oxide and suboxide; salts of *mercury*, *silver*, and *gold*, are reduced to the metallic state. Salts of oxide

of tin decompose *sulphurous acid*, a salt of the binoxide and bisulphide of tin being formed at the same time.

$$6 \text{ Sn O} + 2 \text{ S O}_2 = 5 \text{ Sn O}_2 + \text{Sn S}_2.$$

BINOXIDE OF TIN.

$\text{Sn O}_2.$
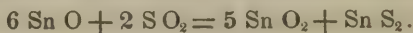
Binoxide of tin exists under two different modifications, that is, insoluble and soluble, the properties of which may be traced even in their compounds with acids.

The insoluble modification exists in the hydrate of binoxide of tin, HO, Sn O_2, which is formed by the action of nitric acid upon metallic tin. In this state binoxide of tin combines with acids forming salts, which are quite insoluble in acids; when separated from the excess of acid, however, they dissolve in water, but from this solution they are again precipitated by the acid. After ignition this binoxide no longer combines with acids.

The soluble modification is always formed by fusing the insoluble one with an excess of *caustic* or *carbonated alkali*. It is easily soluble in acids. *Caustic alkalies* precipitate from this solution soluble hydrate of binoxide.

Hydrosulphuric acid precipitates from salts of binoxide of tin, particularly on gently beating, yellow bisulphide of tin, which is soluble in sulphide of ammonium, in ammonia, potassa, and carbonate of potassa.

Ammonia and *potassa* produce a white precipitate of hydrate of binoxide, readily soluble in an excess of the precipitant, if the salt contains the soluble modifi-

cation; but difficultly soluble or insoluble, if it contains the insoluble one.

Carbonate of potassa produces the same precipitate as potassa or ammonia, which is also soluble in an excess of the precipitant; all the binoxide of tin, however, is separated again completely from this solution by boiling.

When heated on charcoal with *carbonate of soda* and *cyanide of potassium*, in the inner flame of the blow-pipe, all tin compounds yield globules of ductile metal, without incrustation of oxide.

c. OXIDES OF ARSENIC.

ARSENIOUS ACID.

$$As\ O_3.$$

Arsenic, when heated in contact with the atmosphere, is transformed into arsenious acid with a characteristic garlic-odor. If the experiment be conducted in a glass tube open at both ends and held obliquely, the arsenious acid is deposited on the cool surface of the upper part of the tube, in the form of a white incrustation. Strong nitric acid or nitro-hydrochloric acid converts arsenic, and arsenious acid, into arsenic acid, $As\ O_5$; the same acid is formed by the action of these oxidising agents upon sulphides of arsenic, sulphuric acid being formed at the same time.

Arsenious acid is either white like porcelain, or transparent like glass. The vapor of this compound is perfectly inodorous; the characteristic smell being perceptible only if arsenious acid be evaporated on charcoal

or iron, or in general on some support exercising a reducing effect. Arsenious acid is slightly soluble in water, but is readily soluble in hydrochloric acid and the fixed caustic alkalies.

A solution of arsenious acid in water acquires only a yellow tint by the action of *hydrosulphuric acid*, but in the presence of free acid (hydrochloric acid) the arsenic is completely precipitated in the form of tersulphide of arsenic (sulpharsenious acid), As S_3. The deportment of tersulphide of arsenic with other bodies is so important in analytical chemistry that we must treat of it somewhat in detail.

Tersulphide of arsenic, especially when recently precipitated, is soluble in *caustic* and *carbonated alkalies*, and in *alkaline sulphides;* it dissolves readily in boiling *nitric acid*, but not in *hydrochloric acid.*

The solution of tersulphide of arsenic in potassa contains arsenite of potassa and a double compound, sulpharsenite of sulphide of potassium.

$$2 \text{ As S}^3 + 5 \text{ KO} = 2 \text{ KO, As O}_3 + 3 \text{ KS, As S}_3.$$

When tersulphide of arsenic is fused with a *carbonated alkali* the same decomposition takes place. On passing the vapors of tersulphide of arsenic over *lime* heated to redness, sulphide of arsenic and calcium, and arseniate of lime are formed, with separation of arsenic.

If in this experiment the lime or carbonated alkali be mixed with *charcoal*, this charcoal oxidises at the expense of the alkali, the metal of which being liberated combines with the sulphur of the sulphide of arsenic. Thus arsenic is set free, the sulphide of the alkali-

metal combining with the sulphide of arsenic remaining undecomposed.

The same deportment is observed on heating a mixture of sulphide of arsenic and *carbonated alkali* in a current of dry *hydrogen gas.*

Tersulphide of arsenic, when fused with *cyanide of potassium*, loses all its sulphur, sulphocyanide of potassium being formed with the liberation of arsenic.

$$2 \text{ As S}_3 + 3 \text{ K Cy} = 3 \text{ K Cy S}_2 + 2 \text{ As.}$$

The reduction of arsenic by means of *carbonate of soda* or *cyanide of potassium*,* is very well effected by introducing the mixture into a glass tube drawn out into a long and open point, and heating to redness, while a stream of dry hydrogen or carbonic acid gas (the latter in the case of cyanide of potassium) is passed over it. Arsenic is deposited on the cold surface of the narrow part of the tube in the form of a black mirror.

A similar reduction takes place on strongly heating in a thin tube, the sealed end of which is blown out to a small bulb, sulphides of arsenic, arsenites or arseniates with a mixture of equal parts of *cyanide of potassium* and dry *carbonate of soda.* In this experiment the oxides of arsenic yield cyanate of potassa.

$$2 \text{ As O}_3 + 3 \text{ K Cy} = 3 \text{ (K O, Cy O)} + 2 \text{ As.}$$
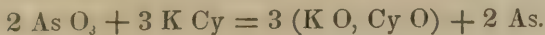
When a solution of tersulphide of arsenic in sulphide of potassium is mixed with a salt of *copper*, *lead*, or

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* The experiment succeeds best by using 1 part of sulphide of arsenic and 12 parts of a mixture of 1 part of cyanide of potassium and 3 parts of carbonate of soda well dried.

silver, these metals are converted into sulphides, arsenite of potassa being formed.

$$K S, As S_3 + 4 Ag O = 4 Ag S + K O, As O_3.$$
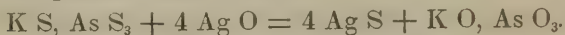
Quinquisulphide of arsenic, when treated in this manner, yields arseniate of potassa.

$$K S, As S_5 + 6 Ag O = 6 Ag S + K O, As O_5.$$

Nitrate of silver produces in n e u t r a l salts of arsenious acid a yellow precipitate of arsenite of silver, $2 Ag O, As O_3$, soluble in nitric acid and ammonia.

Sulphate of copper precipitates yellowish-green arsenite of copper, $2 Cu O, As O_3$.

Lime water, or soluble *lime-salts*, precipitate white arsenite of lime, $2 Ca O, As O_3$.

All insoluble salts of arsenious acid dissolve in ammoniacal salts; the presence of which prevents therefore the formation of the above-mentioned precipitates.

Arsenite of potassa, when heated with *sulphate of copper* and an excess of *caustic potassa*, is decomposed into arseniate of potassa and suboxide of copper.

$$K O, As O_3 + 4 (Cu O, SO_3) + 4 K O = K O, As O_5 + 2 Cu_2O + 4 (K O, S O_3).$$
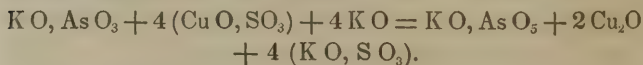
The precipitate of red suboxide of copper, which (on application of a gentle heat) separates from a solution of arsenious acid in potassa, to which a few drops of *sulphate of copper* have been added, will be perceptible, even if the quantity of arsenious acid be very minute.

Arsenic combines with hydrogen when in the nascent state, forming terhydride of arsenic (arsenietted hydrogen), $As H_3$. This is effected by bringing together *arsenious acid*, or an *arsenite*, with *zinc, water*, and *sulphuric* or *hydrochloric acid*.

$$6 Zn + 3 H O + As O_3 + 6 S O_3 = 6 (Zn O, S O_3) + As H_3.$$
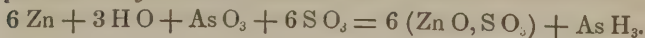
Terhydride of arsenic is a violent poison, and pos-
sesses an exceedingly offensive odor. When kindled
in contact with the atmosphere it burns with a bluish-
white flame, *water* and *arsenious acid* being formed;
when, however, free access of the air is prevented, only
the hydrogen is oxidised, with deposition of *arsenic*.
The same separation of arsenic takes place when ter-
hydride of arsenic is passed through a glass tube, a
part of the tube being heated to redness by a spirit-
lamp. By this means the smallest trace of any oxygen
compound of arsenic may be detected. For this pur-
pose some zinc and dilute sulphuric acid are introduced
into an evolution-flask, into which are fitted air-tight,
by means of a cork, a funnel-tube and a glass tube
bent into a right angle and drawn out into a narrow
open point. After some minutes, when all the amos-
pheric air in the apparatus is displaced by the evolved
hydrogen, the gas issuing from the narrow aperture
may safely be kindled. Then, by depressing a cold
porcelain surface into the flame, the absence of arsenic
in either zinc or sulphuric acid is first ascertained by
the surface remaining completely white. The solu-
tion to be examined for arsenic is now added through
the funnel-tube, and the hydrogen gas again kindled.
If the slightest quantity of an oxygen compound of
arsenic be present the porcelain surface will now be
covered with metallic mirrors of a brown or steel-grey
color, which are soluble in boiling nitric acid.

When the terhydride of arsenic disengaged in this
manner is passed through a long glass tube of difficultly
fusing glass, drawn out to a similar point and heated
in the middle part to redness, a circular mirror of arse-

nic is deposited in the narrow part of the tube. The tube should now be cut off, and the point sealed; on heating the deposit it is converted by the oxygen contained in the tube into arsenious acid, which may be dissolved in hot water, and tested by the above given reactions.

Under the same circumstances antimony produces a similar mirror, which has however a lighter color than that of arsenic. In order to distinguish them, the incrustations are heated in an atmosphere of dry *hydrosulphuric* acid; both deposits are converted into sulphides, but the sulphides of arsenic are *yellow*, while those of antimony are *red* or *grey*, and less volatile than the former. A stream of *hydrochloric acid* converts the sulphides of antimony into chlorides, which are volatilised, while the sulphides of arsenic remain. These may be distinguished from sulphur by their solubility in ammonia.

The oxygen compounds of arsenic may also be reduced by *charcoal*.

For this purpose a glass tube is drawn out to a thin point of half an inch in length and sealed; into this a small piece of arsenious acid, and then a thin charcoal splinter is introduced. On heating, first this splinter, and then the acid, the latter is deprived of its oxygen, and a circular mirror of arsenic is deposited on the cooler part of the tube.

Compounds of arsenious acid are treated in the same manner with a mixture of *charcoal* and *carbonate of soda* or *boracic acid;* arsenic, however, under these circumstances, is only volatilised, if the metallic basis of the arsenite does not form with arsenic a compound which resists the action of heat.

Metallic copper, when introduced into a solution of arsenious acid, becomes covered with a grey metallic coat, which, by boiling, separates in black scales. This reaction takes place even when the solution of arsenious acid is extremely dilute.

On heating arsenious acid with a dry *acetate* and *hydrate of potassa*, oxide of kakodyl is disengaged, by the peculiar insupportable smell of which compound even very minute traces of arsenious acid may be detected.

$$2\,(K\,O,C_4H_3O_3) + 2\,K\,O + As\,O_3 = C_4H_6\,As\,O + 4(K\,O,CO_2).$$

Acetate of potassa.   Oxide of kakodyl.

ARSENIC ACID.

As O₅.
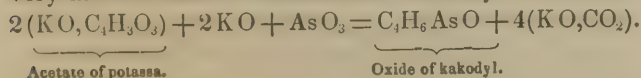
Arsenic acid deliquesces in contact with the atmosphere; it volatilises only at a very strong heat, being decomposed into arsenious acid and oxygen. Arseniates insoluble in water dissolve in hydrochloric acid.

Hydrosulphuric acid produces in an acid solution of arsenic acid *only very slowly* a precipitate of yellow quinquisulphide, As S₅, the chemical comportment of which is similar to that of the tersulphide (*v. supra*).

Arsenic acid is converted into arsenious acid by *sulphurous acid:*

$$As\,O_5 + 2\,S\,O_2 = As\,O_3 + 2\,S\,O_3\,,$$
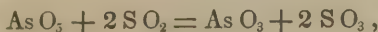
which property may be used for obtaining immediately a precipitate with *hydrosulphuric acid.*

Lime water produces in a neutral solution of an arseniate a white precipitate, 2 Ca O, H O, As O₅.

Nitrate of silver produces a reddish-brown precipitate, $3\,AgO,\,AsO_5$.

Sulphate of copper a greenish-blue precipitate, $2\,CuO,\,HO,\,AsO_5$.

Free *ammonia* prevents the formation of these precipitates, and they are all insoluble in *nitric acid.*

On exposing an arsenic compound on charcoal to the inner flame of the blowpipe, the peculiar garlic smell of suboxide of arsenic is disengaged, by which even very minute traces of arsenic may be recognised.

In qualitative analysis the three last bodies (antimony, tin, and arsenic) are always obtained together in the form of their highest sulphides SbS_5, SnS_2, AsS_5, on precipitating the solution in sulphide of ammonium by means of an acid.

In testing for these three elements in this precipitate the following method is generally adopted.

The dry sulphides are fused with *nitre* and *carbonate of potassa* or *carbonate of soda ;* by this process they are converted into the corresponding oxides, SbO_5, SnO_2, AsO_5, which combine with the alkali, all the sulphur being oxidised into sulphuric acid.

On treating the fused mass with cold water we have in the

SOLUTION,	RESIDUE,
Arseniate of potassa, sulphate of potassa, and a small quantity of antimoniate of potassa, and stannate of potassa.	Antimoniate of potassa and stannate of potassa.

On neutralising the aqueous solution by nitric acid the small quantity of antimonic acid and binoxide of tin (stannic acid) is precipitated; the filtrate is tested for arsenic acid by addition of *nitrate of silver* to the liquid, first carefully neutralised by ammonia, as also by throwing down by *acetate of lead*, and examining the white precipitate (sulphate and arseniate of lead) before the blowpipe.

The white residue which remains, after exhaustion by water, contains binoxide of tin, or antimonic acid, or both. This residue is reduced by means of *cyanide of potassium* before the blowpipe, or when obtained in a larger quantity in a porcelain crucible over the spirit-lamp. If the metallic globule produced in this manner be brittle it is antimony, if it be ductile it is tin.

A globule containing both antimony and tin, is converted into the oxides of these two metals by the action of *nitric acid*. On boiling these mixed oxides (carefully washed) in a solution of *tartaric acid* or *bitrate of potassa*, teroxide of antimony is dissolved and may be detected by *hydrosulphuric acid*. Binoxide of tin is not affected by tartaric acid.

A careful comparison of the above described reactions of these three elements will afford further means of ascertaining their presence.

The following remark may still be useful: — If an alloy of these three elements be oxidised by means of nitric acid the greater part of the arsenic becomes insoluble as arseniate of antimony. On fusing the sulphides with *nitre* and *carbonate of soda* this difficulty does not occur.

2. *SUBDIVISION.*

a. BINOXIDE OF PLATINUM.

Pt O_2.

Platinum is insoluble in hydrochloric acid and nitric acid; it dissolves, however, in nitro-hydrochloric acid, forming a reddish-brown solution, which contains the bichloride, Pt Cl_2, corresponding to the binoxide.

Hydrosulphuric acid produces in this solution a brownish-black precipitate of bisulphide of platinum, Pt S_2; a gentle heat promotes the formation of this precipitate, which is insoluble in nitric acid and hydrochloric acid, but dissolves in nitro-hydrochloric acid and in sulphide of ammonium.

Salts of potassa and *ammonia*, especially *chloride of potassium* and *chloride of ammonium*, precipitate yellow crystalline double salts, which are but slightly soluble in water, and even less in alcohol.

Chloride of tin, in the presence of free hydrochloric acid, imparts to a solution of platinum a dark reddish-brown color.

[*b.* BINOXIDE OF IRIDIUM.]

Ir O_2.

Iridium dissolves, but very slowly, in nitro-hydrochloric acid, more easily when alloyed with platinum. The dark reddish-brown solution contains bichloride of iridium, Ir Cl_2.

Hydrosulphuric acid first discolors the solutions of iridium, and then precipitates brown bisulphide of iridium, which is soluble in sulphide of ammonium.

The same discoloration, partly with, partly without precipitation, is produced by a great number of reagents, such as *sulphate of oxide of iron, iodide of potassium, oxalic acid, cyanide of potassium*, etc.

The compounds of bichloride of iridium with the alkaline chlorides are dark-red, almost black.

c. TEROXIDE OF GOLD.

$Au\ O_3$.

Gold is insoluble in hydrochloric acid and in nitric acid; it dissolves, however, easily in nitro-hydrochloric acid, forming a terchloride, $Au\ Cl_3$, of a yellow color, which is still perceptible even in very dilute solutions.

Most of the common metals, and also *silver, palladium*, and *platinum* reduce the gold from these solutions partly to the state of metal, which appears either as a shining coating or as a brown powder, partly to a particular compound of a purple color.

The most important reducing agents of gold are *salts of oxide of iron, oxalic acid*, and *chloride of tin*.

Salts of oxide of iron and *oxalic acid* precipitate metallic gold in the form of a brown impalpable powder, which on being rubbed with a hard body assumes a golden lustre.

$$Au\ Cl_3 + 6\ (Fe\ O, S\ O_3) = Au + 2\ (Fe_2\ O_3, 3\ S\ O_3) + Fe_2\ Cl_3.$$
$$Au\ Cl_3 + 3\ (H\ O, C_2\ O_3) = Au + 3\ H\ Cl + 6\ CO_2.$$
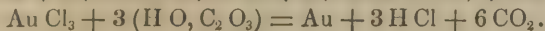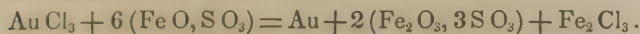
Chloride of tin, containing a little *bichloride* (addition of a drop of nitric acid), produces even in a very dilute solution of gold a purple precipitate, which probably is a compound of a lower oxide of gold and sesquioxide of tin.

6

3. *SUBDIVISION.*

[*a.* SELENIOUS ACID.]

$$Se\ O_2.$$

Selenium on being heated in contact with the atmosphere is converted first into oxide of selenium, diffusing a penetrating horseradish-like odor, and then into selenious acid.

Free selenious acid and selenites, after the addition of hydrochloric acid, are reduced into selenium by *hydrosulphuric acid* and *sulphurous acid.* The precipitate obtained by hydrosulphuric acid is reddish-yellow; the precipitate by sulphurous acid is red when produced in the cold, and grey when produced in a boiling solution.

The same reactions are exhibited by selenic acid, $Se\ O_3$, or seleniates after boiling with hydrochloric acid, by which selenious acid is produced with evolution of chlorine.

[*b.* TELLUROUS ACID.]

$$Te\ O_2.$$

Solutions of tellurium in mineral acids become turbid on the addition of much *water.*

The *caustic alkalies* and *their carbonates* throw down from these solutions a white hydrate of tellurous acid, which dissolves when heated with an excess of the precipitant.

Hydrosulphuric acid precipitates black bisulphide of tellurium, soluble in sulphide of ammonium.

Tellurous acid is reduced on being boiled with *sul-*

phurous acid or *alkaline sulphates*, with precipitation of black flocculent tellurium; this precipitate is the more rapid and complete the more concentrated the solution.

Tellurium is also precipitated by *chloride of tin* and *sulphate of oxide of iron* as a black powder, which on being rubbed assumes metallic lustre.

When heated in contact with the air, tellurium burns with a blue flame, exhibiting a greenish edge, and evolving white fumes of a disagreeable feebly acidulous odor.

Telluric acid, the highest oxide of tellurium, is formed on fusing tellurous acid with *nitre*. The salts of this acid are reduced to tellurites by ignition, and to tellurium by boiling with a mixture of *hydrochloric* and *sulphurous acid.*

4. *SUBDIVISION.*

[a. OXIDES OF TUNGSTEN.]

$$W O_2, W O_3.$$
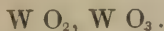
The lower oxides of this metal, on being heated in contact with the atmosphere, or on being treated with nitric acid, are converted into tungstic acid, $W O_3$. On fusing minerals containing tungsten with *nitre* and *carbonate of soda*, and treating the fused mass with water, an alkaline tungstate is obtained in solution; free mineral acids precipitate from this solution, hydrate of tungstic acid insoluble in an excess of the precipitant (phosphoric acid excepted).

Tungstic acid is not completely precipitated by mineral acids; the acid solution still contains a quantity of

tungsten. *Zinc* produces in these acid solutions (with exception of the nitric acid solution) a beautiful blue color, owing to the formation of oxide of tungsten.

Sulphide of tungsten is precipitated only when a tungstate is decomposed by acids in presence of *sulphide of ammonium*.

The oxides of tungsten, when perfectly pure, impart to *phosphorus salt* in the inner flame of the blowpipe a beautiful *blue* color, which disappears in the outer flame; in the presence of iron the bead assumes a *blood-red* color in the inner flame.

[b. OXIDES OF MOLYBDENUM.]

Mo O, Mo O_2, Mo O_3.
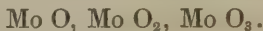
Molybdenum and its inferior oxides, as also sulphide of molybdenum, are converted into molybdic acid by continuous ignition in contact with air, but quicker by treatment with oxidising agents.

The alkaline molybdates (obtained by fusing a molybdenum compound with *nitre* and *carbonate of soda*), when decomposed by a mineral acid, yield a white precipitate of molybdic acid, which is, however, soluble in an excess of the precipitant.

In a solution of molybdic acid containing free hydrochloric acid, *zinc* or *tin* produce a blue color, which after some time becomes green, and at last black.

Hydrosulphuric acid, when added in excess to an acid solution of molybdic acid, produces, after some time, a brown precipitate of sulphide of molybdenum, the supernatant liquid remaining blue or green. On adding only a small quantity of hydrosulphuric acid,

no precipitate is produced, but the liquid assumes a blue color.

Sulphide of molybdenum is also produced, when a molybdate is decomposed by acids in presence of *sulphide of ammonium*.

The oxides of molybdenum impart to *phosphorus salt*, in the inner blowpipe-flame, a fine *green* color, which becomes more perceptible on cooling; with *borax* they produce, in the inner blowpipe-flame, a *brownish-red* bead.

[c. OXIDES OF VANADIUM.]
$V O.$ $V O_3$.
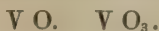
Vanadium, in the reactions of its compounds, most resembles tungsten, molybdenum, and chromium.

Most of the salts of oxide of vanadium are blue or green.

From their solution *fixed caustic alkalies* precipitate a grey-white hydrate, soluble in an excess of the precipitant forming a grey or brown solution, but insoluble in ammonia.

Hydrosulphuric acid produces no precipitate.

Sulphide of ammonium, however, throws down a brownish-black precipitate, which dissolves in an excess of the precipitant, the solution being of a dark purple color.

The vanadates possess a red or yellow color, which disappears on heating. Vanadic acid dissolves in mineral acids, and is reduced in these solutions by *hydrosulphuric acid* or *organic substances* to blue oxide, which remains in solution.

6 *

Sulphide of ammonium precipitates brown tersulphide of vanadium, $Va\,S_3$, which dissolves in an excess of the precipitant, forming a brown liquid.

Ferrocyanide of potassium produces a fine green precipitate.

Chloride of ammonium forms in solutions of vanadic acid a white flocculent precipitate of vanadate of ammonia, which is quite insoluble in an excess of chloride of ammonium.

The oxides of vanadium, when heated with *borax* or *phosphorus salt*, produce in the outer blowpipe flame a *yellow*, in the inner flame a beautiful *green* bead, which becomes yellow again, and even colorless, when exposed to the oxidising flame.

SECTION II.

BEHAVIOR OF THE ACIDS WITH REAGENTS.

I.—ACIDS OF SULPHUR AND SELENIUM.

HYDROSULPHURIC ACID.

H S.

HYDROSULPHURIC ACID (sulphuretted hydrogen) is a colorless gas, which becomes liquid when exposed to strong pressure.

Hydrosulphuric acid is easily recognised by its characteristic disagreeable odor (that of rotten eggs). In contact with the air it burns with a blue flame, sulphurous acid and water being formed. Hydrosulphuric acid is soluble in cold water, 3 vols. of water absorbing 1 vol. of gas (hydrosulphuric acid-water).

With most metallic oxides hydrosulphuric acid changes sulphur for oxygen, water and sulphides being formed, which may often be distinguished by their peculiar color. Only the alkaline earths proper, and the oxides of chromium, titanium, and tantalum, do not exchange their oxygen for sulphur in the moist way.

The compounds of sulphur with the metals of the alkalies and the alkaline earths are soluble in water, whilst those with heavy metals are insoluble. On exposure to high temperatures the sulphides of different metals exhibit a varying comportment. Tersulphide of gold, ex. gr., when ignited loses all its sulphur, pure metal remaining behind; bisulphide of tin, $Sn S_2$, is transformed into sulphide, $Sn S$, with evolution of half its sulphur; sulphide of zinc is not altered by heat.

When heated in contact with the air (in a glass tube open at both ends) most sulphides evolve sulphurous acid, leaving in some cases metal (silver), in other cases oxide (antimony, tin, bismuth). The alkaline sulphides are converted by this process into sulphates.

On fusing a sulphide upon charcoal with carbonate of soda, a mass is obtained, which when moistened with water produces a brownish black spot upon a bright silver surface, and disengages hydrosulphuric acid upon addition of an acid.

Most of the sulphides are decomposed by *nitric acid* with the formation of oxide, sulphuric acid, and, unless the acid was very concentrated, with separation of sulphur.

Nitro-hydrochloric acid acts in the same manner, but with more energy.

Sulphides are also decomposed by *chlorine*, the corresponding chlorides of the metal and chloride of sulphur being formed.

They are soluble in *hydrochloric acid* with disengagement of hydrosulphuric acid.

A solution of hydrosulphuric acid in water is de-

composed by *sulphurous acid*, water being formed and sulphur separated.

$$SO_2 + 2\,HS = 2\,HO + 3\,S.$$

Chlorine, bromine, and *iodine* effect a similar decomposition, the hydrogen-acids of these elements being formed, with separation of sulphur.

Hydrosulphuric acid is decomposed in a similar manner by *hypochlorous acid, nitric acid, iodic acid, bromic acid, chromic acid* and *sesquioxide of iron,* etc. In most of these cases a certain quantity of the sulphur separated is converted into sulphuric acid.

A solution of hydrosulphuric acid in water is decomposed even by contact with the *air,* water being formed with separation of highly divided sulphur.

Traces of hydrosulphuric acid, no longer perceptible by the smell, are detected by *acetate of lead,* or by paper moistened with a solution of this salt, when in a mixture of gases. The paper becomes covered with a brownish black shining coating.

[HYDROSELENIC ACID.]

H Se.

Hydroselenic acid, in its chemical deportment, very much resembles hydrosulphuric acid; selenides are however easily distinguished from sulphides by the horseradish-like odor they disengage on being heated in contact with the air.

SULPHURIC ACID.

HO, SO_3.
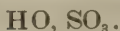
Anhydrous sulphuric acid forms a white crystalline mass resembling asbestos, and disengaging dense white fumes when in contact with air. In combination with one equivalent of water it forms common sulphuric acid (oil of vitriol) an oily liquid, the boiling point of which is 300° C. (572° Fahr.) Anhydrous sulphuric acid, as well as oil of vitriol, produce a very high degree of heat when mixed with water. Organic substances are destroyed by the action of concentrated sulphuric acid setting free their carbon (blackening of organic substances by sulphuric acid). On supporting the action by the application of heat the carbon is oxidised at the expense of the sulphuric acid, carbonic acid and sulphurous acid being formed : —

$$2 SO_3 + C = CO_2 + 2 SO_2.$$
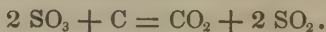
Sulphuric acid possesses the strongest affinity for bases, it displaces all other acids in their saline compounds. Almost all the neutral and acid salts of sulphuric acid are soluble in water; sulphate of lime however is slightly soluble; sulphate of baryta, strontia, and lead, are insoluble or nearly so. The soluble salts of these oxides (especially of baryta), are therefore used as tests for sulphuric acid.

Sulphate of baryta, BaO, SO_3, which is formed immediately on addition of *chloride of barium* to a soluble sulphate, is completely insoluble in nitric and hydrochloric acids. In testing a solution for sulphuric acid by means of a baryta salt, care should be taken that

the liquid does not contain too much nitric or hydro-
chloric acid, as salts of baryta, which easily dissolve
in water, are almost insoluble in nitric and hydrochlo-
ric   ids.   The white precipitate which forms on addi-
t   hese acids to a soluble baryta salt, is however
e   dissolved by water.

The compounds of sulphuric acid with the fixed al-
kalies, with the alkaline earths and oxide of lead, are
not decomposed on being ignited alone; all the other
sulphates are destroyed by ignition, sulphuric acid
and sulphurous acid or oxygen, according to the nature
of the base, being disengaged.

All the sulphates are decomposed on being ignited
with charcoal; if in this decomposition an alkali (car-
bonate of soda, cyanide of potassium) be present, an al-
kaline sulphide is produced which disengages hydro-
sulphuric acid, when treated with an acid, and blackens
a bright silver surface on being moistened with water.
The same behavior is exhibited by the compounds of
sulphurous acid, and in general all the acids of sulphur
(detection of sulphates before the blowpipe).

The sulphates insoluble in water and acids, are com-
pletely decomposed by fusion with an alkaline carbo-
nate, but only partially on boiling with a solution of
the alkali water; in the filtered liquid saturated with
hydrochloric acid a precipitate of sulphate of baryta is
produced on addition of a soluble baryta salt.

[SELENIC ACID.]

$$HO, SeO_3.$$

Selenic acid and seleniates very much resemble sul-

phuric acid and sulphates, in their chemical deportment; seleniates however are decomposed on boiling with *hydrochloric acid*, selenious acid being formed with disengagement of chlorine; the decomposed seleniate now possesses the property of decolorising *sulphindigotic acid ;* it is precipitated by *sulphurous acid*, or *hydrosulphuric acid* (v. p. 70), but no longer by *chloride of barium.* On being exposed to the inner flame of the blowpipe with *phosphorus salt* or *carbonate of soda*, all compounds of selenium disengage a characteristic horseradish-like odor.

SULPHUROUS ACID.

$$SO_2.$$

Sulphurous acid is formed on burning sulphur in contact with the air, at the common temperature it is a transparent gas, which easily dissolves in water; both as gas, and in solution, it possesses the well-known disagreeable odor of burning sulphur. Among the neutral compounds of sulphurous acid, the alkaline sulphites only are soluble in water, but all its acid salts are soluble.

Most of the sulphites on being heated are converted into a mixture of sulphide and sulphate : —

$$4 (PbO, SO_2) = 3 (PbO, SO_3) + PbS.$$

By the action of *chlorine, nitric acid* or fusing *nitre*, sulphites are converted into neutral sulphates.

On boiling a solution of a sulphite with a *baryta salt* and *nitric acid*, a precipitate of insoluble sulphate of baryta is formed.

Nitrate of silver produces in a solution of a sulphite a precipitate, which first is white, but becomes black on digestion or on gently heating, the metal being reduced with formation of sulphuric acid :—

$$Ag\,O, SO_2 = Ag + SO_3.$$
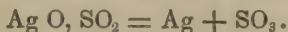
Chloride of tin, to which hydrochloric acid has been added, produces even in a very dilute solution of sulphurous acid a brown precipitate of sulphide of tin; in the presence of a large quantity of sulphurous acid, the color of the precipitate is yellow.

Sulphites, when in contact with *metallic zinc* and *hydrochloric acid* or *sulphuric acid* evolve hydrosulphuric acid :—

$$SO_2 + HO + 3\,Zn + 3\,SO_3 = 3\,(Zn\,O, SO_3) + HS.$$
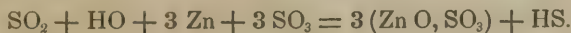
Chloride of barium and of *calcium* produce white precipitates in solution of neutral sulphites; these precipitates are readily soluble in hydrochloric acid.

[SELENIOUS ACID.] (v. p. 62.)

$$Se\,O_2.$$

[HYPOSULPHUROUS ACID.]

$$S_2\,O_2.$$

The compounds of this acid with alkalies and alkaline earths (the baryta salt excepted) are readily soluble, and possess the property of dissolving chloride of silver, when freshly precipitated.

By the action of *nitric acid*, the salts of this acid are converted into acid sulphates.

$$KO, S_2O_2 + 4O = KO, 2\,SO_3.$$

From the nitric acid.

7

Hydrochloric acid decomposes them with evolution of sulphurous acid and separation of sulphur.

$$KO, S_2O_2 + HCl = KCl + HO + SO_2 + S.$$

Hyposulphites on being boiled with *salts of copper* or *silver* are converted into sulphates; sulphides of copper and silver being formed.

$$KO, S_2O_2 + AgO, NO_5 = KO, SO_3 + AgS + NO_5.$$

[HYPOSULPHURIC ACID.]

$$S_2O_5.$$
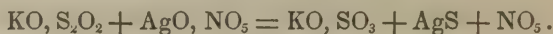
The salts of this acid are soluble in water; on being heated alone or with hydrochloric acid they are converted into sulphates, sulphurous acid being disengaged without separation of sulphur.

$$KO, S_2O_5 = KO, SO_3 + SO_2.$$

The acids S_3O_5 and S_4O_5 only recently discovered, are likewise converted into sulphates with disengagement of sulphurous acid; at the same time, however, a separation of sulphur takes place.

II. — CHROMIC ACID.

$$Cr O_3.$$

Chromic acid forms scarlet red needles, which deliquesce in the air; its salts are yellow or red. The alkaline chromates are soluble in water; all the chromates dissolve in nitric acid. The yellow solution of a neutral chromate assumes a dark red color on addition of a mineral acid, an acid chromate being formed or chromic acid separated.

Baryta salts produce in soluble chromates a pale yellow precipitate of chromate of baryta, BaO, CrO_3.

Lead salts precipitate lemon-yellow chromate of lead, PbO, CrO_3.

Bismuth salts throw down chromate of bismuth, $Bi O_3$, $3 CrO_3$, of the same color.

Silver salts precipitate purple red chromate of silver, AgO, $Cr O$.

Subsalts of mercury produce a brick-red precipitate of subchromate of mercury, Hg_2O, CrO_3.

All these precipitates are soluble in nitric acid, chromate of lead is also soluble in potassa; chromic acid is reduced to sesquioxide of chromium by *hydrosulphuric acid* and *sulphurous acid,* and also by *oxalic, tartaric* and *citric acids ;* by *metallic zinc* and by *alcohol* in the presence of a free acid.

In reducing chromic acid by hydrosulphuric acid, sulphur is separated and sulphuric acid as a secondary product formed; in employing sulphurous acid, sulphuric and hyposulphuric acids are produced; in effecting the deoxidation by means of an organic acid, carbonic acid is disengaged. On treating a neutral chromate with hydrosulphuric acid, a greenish grey mixture of sulphur and sesquioxide of chromium is precipitated ; in the presence of a free acid sesquioxide of chromium remains in solution, only sulphur being precipitated.*

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* By this deportment the presence of chromic acid is indicated, when examining for the bases ; in the acid solution treated with hydrosulphuric acid, chromium is contained in the form of sesquioxide.

III. — ACIDS OF PHOSPHORUS.

PHOSPHORIC ACID.

$$3 \text{ HO, } PO_5.$$

Phosphoric acid, when anhydrous, appears in white flakes; the hydrate forms a glassy mass; both are very deliquescent. The alkaline phosphates readily dissolve in water; all the other salts are insoluble in water, but dissolve in dilute nitric acid. The phosphates with fixed bases, are not decomposed by heat. Salts of phosphoric acid, which are insoluble in water are only partially decomposed by fusion with the caustic fixed alkalies or their carbonates. Alkaline phosphates, with one equivalent of fixed base, possess an acid reaction; those with two or three equivalents, exhibit an alkaline reaction. The latter salts yield with *lime* and *baryta salts* white precipitates, which are soluble in *hydrochloric acid, nitric acid*, and even in *acetic acid.*

Soluble *magnesia salts* give with phosphate of soda, $2 \text{ NaO, HO, } PO_5$, a crystalline precipitate, which appears only after some time. With the soda salt, $3 \text{ NaO, } PO_5$, all the magnesia is immediately thrown down as a white precipitate. In the presence of free ammonia, magnesia salts produce even in very dilute solutions of phosphates, with 2 equivalents of fixed base, a white precipitate of phosphate of magnesia and ammonia, $2 \text{ MgO, NH}_4\text{O, } PO_5 + 12 \text{ aq.}$

Nitrate of silver produces in solutions of the common phosphates (with 3 equivalents of base) lemon-yellow phosphate of silver, $3\text{AgO, } PO_5$, which is with difficulty

soluble in acetic acid; if the tribasic phosphate contained only 1 or 2 equivalents of fixed base, it yields, after ignition, a white precipitate with nitrate of silver $AgO, PO_5,$ or $2\ AgO, PO_5$.

Lead salts produce a white precipitate, which is almost insoluble in acetic acid. This precipitate fuses before the blowpipe into a bead, which on cooling becomes crystalline.

Salts of sesquioxide of iron form in alkaline phosphates an almost white gelatinous precipitate of phosphate of sesquioxide of iron, which is insoluble in acetic acid.

On adding to the hydrochloric acid solution of a phosphate insoluble in water, (ex. g., the phosphate of an alkaline earth,) a sufficient quantity of an *alkaline acetate* and *sesquichloride of iron*, a precipitate of phosphate of sesquioxide of iron is obtained. In this way all the phosphoric acid may be separated from a liquid.

On heating a dry phosphate in a glass-tube with *potassium*, separating the excess of potassium by means of mercury and moistening gently the residue, (it is sufficient to blow moist air into the tube,) terhydride of phosphorus (phosphoretted hydrogen) is disengaged, which may be easily recognised by its peculiar odor.

On fusing a phosphate with *boracic acid* upon charcoal before the blowpipe and introducing a fine *iron-wire* into the fused mass, a brittle bead of magnetic phosphide of iron is produced by heating strongly in the inner flame.

7*

[PHOSPHOROUS ACID.]

PO_3.

[HYPOPHOSPHOROUS ACID.]

PO.

The alkaline phosphites are soluble in water; most compounds of phosphorous acid with the alkaline earths or the other oxides are insoluble or difficultly soluble.

Dilute solutions of *magnesia* are not precipitated by soluble phosphites, even in the presence of *chloride of ammonium* and *ammonia*.

Oxide of silver is decomposed by phosphorous acid, the metal being reduced and phosphoric acid formed.

On heating, most phosphites are converted into phosphates with evolution of hydrogen.

All compounds of hypophosphorous acid are soluble in water; when heated, they are converted into phosphates, inflammable terhydride of phosphorus being disengaged.

On boiling a solution of a hypophosphite with an excess of alkali, hydrogen is disengaged, an alkaline phosphate remaining.

IV. — ACIDS OF NITROGEN.

NITRIC ACID.

HO, NO_5.
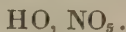
Pure hydrate of nitric acid is a colorless liquid, diffusing white fumes of a pungent odor, when in contact with the atmosphere. If the nitric acid contains nitrous

acid these fumes are yellow. Nitric acid oxidises all the metals with the exception of platinum, rhodium, gold, titanium, and tantalum, binoxide of nitrogen being disengaged, which by absorption of oxygen from the air is converted into red fumes of nitrous acid.

With the exception of binoxide of tin, teroxide of antimony, [tellurous acid and tungstic acid], all oxides are soluble in an excess of nitric acid.

All nitrates are decomposed by ignition, oxygen and nitrogen, or oxygen and an inferior oxide of nitrogen being disengaged, according to the nature of the base. If nitrates are ignited in presence of substances capable of oxidation, these latter combine with the oxygen of the acid, with the evolution of inferior oxides of nitrogen; this act of combination being often so violent that a detonation ensues, as with *cyanide of potassium*, *carbon, phosphorus, sulphur*, &c. Also free nitric acid, when concentrated, acts as a powerful means of oxidation on combustible bodies in general, inorganic and organic.

When treated with an excess of hydrochloric acid, nitrates are converted into chlorides with formation of hyponitric acid and disengagement of free chlorine.

$$KO, NO_5 + 2 \, H \, Cl = K \, Cl + 2 \, HO + NO_4 + Cl.$$
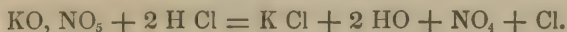
Hence the solubility of *gold leaf* in a solution of a nitrate, which has been heated with hydrochloric acid.

On mixing a solution of a nitrate with half its volume of concentrated sulphuric acid, and adding to this mixture after cooling a concentrated solution of a *salt of oxide of iron*, or some crystals of the *sulphate*, the liquid or the crystals assume a purple, red, or dark

brown color, owing to the formation of a compound of binoxide of nitrogen with the salt of iron.

$$10\,(FeO, SO_3) + 4\,SO_3 + KO, NO_5 = 3\,(Fe_2O_3, 3\,SO_3) + KO,$$
$$SO_3 + 4\,(FeO, SO_3),\,NO_2\,.$$
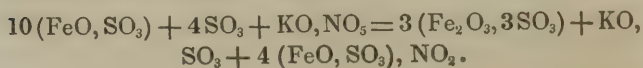
This dark brown compound is destroyed by heat, with disengagement of the binoxide of nitrogen.

On adding to the mixture of the nitrate and sulphuric acid a drop of *sulphindigotic acid* (a solution of indigo in sulphuric acid), the blue color disappears, when heat is applied, passing into yellow.

Nitrates, when heated with *copper turnings*, and moderately dilute sulphuric acid, disengage binoxide of nitrogen, which is converted into nitrous acid by absorption of oxygen from the atmosphere.

$$KO, NO_5 + 3\,Cu + 4\,SO_3 = NO_2 + 3\,(CuO, SO_3) + KO, SO_3\,.$$

b. NITROUS ACID.

$$NO_3\,.$$
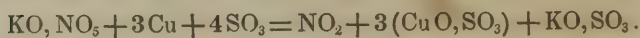
Almost all the compounds of nitrous acid with bases are soluble in water.

Nitrites, when heated with combustible substances, deflagrate like nitrates. By ignition they disengage nitrogen and oxygen; by treatment with concentrated sulphuric acid they evolve binoxide of nitrogen, which in contact with the air forms red vapors of nitrous acid, nitric acid remaining in solution.

Chloride of gold and *nitrate of mercury* are reduced to the metallic state by nitrites.

V.—ACIDS OF THE SALT-RADICALS.

HYDRACIDS.

HYDROCHLORIC ACID (MURIATIC ACID).

H Cl.

Hydrochloric acid is a transparent gas, which in contact with the air by attraction of moisture forms white fumes. This gas possesses a suffocating acid odor, and is absorbed in large quantity by water with evolution of heat (aqueous hydrochloric acid). With the oxides of the metals hydrochloric acid forms water and chlorides.

When heated, chlorides exhibit a varying comportment, some of them are volatile without decomposition (chlorides of tin, antimony, and arsenic) ; some of them are not altered (chlorides of silver, lead, and the alkali metals) ; some of them pass into metal, or (when air is present) into oxide with evolution of chlorine. Most of the chlorides are soluble; chloride of silver, gold and platinum and the subchlorides of mercury, and copper, only are insoluble; chloride of lead is slightly soluble.

Aqueous solutions of hydrochloric acid and chlorides are therefore precipitated by the following reagents.

Nitrate of silver throws them down completely in the form of chloride of silver, Ag Cl, as a white curdy precipitate, which assumes a violet color when exposed to light. This precipitate is absolutely insoluble in nitric acid, but dissolves readily in ammonia (v. oxide of silver, p. 34).

Subnitrate of mercury, Hg_2O, NO_5, separates chlorine likewise completely as white subchloride of mercury, $Hg_2 Cl$ (v. suboxide of mercury, p. 35.)

By *lead salts* chlorides are only imperfectly thrown down, chloride of lead, $Pb Cl$, being slightly soluble in water.

When free hydrochloric acid is heated with peroxides chlorine is set free, distinguished by a yellowish-green color:—

$$2 H Cl + Mn O_2 = Mn Cl + 2 HO + Cl.$$
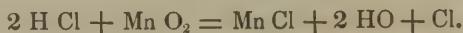
For this purpose the soluble chloride generally is heated with binoxide of manganese and sulphuric acid.

On heating a chloride with *chromate of potassa* and *sulphuric acid*, a brownish red gas is disengaged, which by cooling may be condensed into a blood-red liquid, chromate of chloride of chromium, $Cr Cl_3, 2 CrO_3$.

$$3 (KO, Cr O_3) + 3 Na Cl + 6 HO, SO_3 = Cr Cl_3, 2 CrO_3 + 3 (KO, SO_3) + 3 (NaO, SO_3) + 6 HO.$$
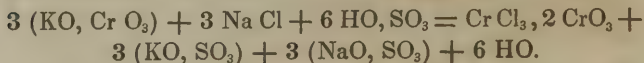
This red liquid, when heated with ammonia, assumes a yellow color, chromate of ammonia being formed.

Chlorides when heated before the blowpipe with a bead of *phosphorus salt*, saturated with *oxide of copper*, impart a *blue* color to the flame.

HYDROBROMIC ACID.

H Br.

Hydrobromic acid and bromides exhibit similar reactions to those of hydrochloric acid and its compounds.

Nitrate of silver precipitates from soluble bromides

yellowish-white bromide of silver, Ag Br, which is insoluble in nitric acid and difficultly soluble in ammonia.

The precipitate which is produced by *subnitrate of mercury* has the same color.

Soluble *lead salts* throw down white *bromide of lead*, Pb Br, which by its insolubility in water may be distinguished from chloride of lead.

Bromides are decomposed by *chlorine, hypochlorites, concentrated sulphuric* and *nitric acids*, bromine being set free, which imparts a yellow or yellowish-red color to the liquid.

$$K\ Br + Cl = K\ Cl + Br.$$
$$K\ Br + 2\ SO_3 = KO, SO_3 + SO_2 + Br.$$
$$3\ K\ Br + 4\ NO_5 = 3\ (KO, NO_5) + NO_2 + 3\ Br.$$
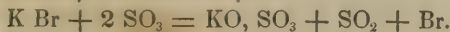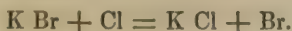
Dilute sulphuric acid, however, disengages hydrobromic acid.

$$K\ Br + HO, SO_3 = KO, SO_3 + H\ Br.$$

Free bromine is soluble in *ether*, and imparts an orange-yellow color to *starch* or *starch-paste*. Small quantities of bromides (even in the presence of chlorides) are therefore easily detected by adding a solution of *chlorine* in water to, or passing a stream of *chlorine* through the liquid to be examined and agitating with *ether*. As soon as the liquids have separated, the solution of bromine in ether is taken off by means of a pipette and agitated with potassa, which withdraws the bromine, bromide of potassium and bromate of potassa being formed.

$$6\ KO + 6\ Br = 5\ K\ Br + KO, BrO_5.$$
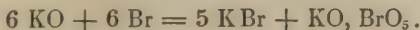
The solution of these two salts is now evaporated to

dryness, and the residue fused (in a silver basin). By this process the bromate is decomposed with evolution of oxygen; the mass containing now only bromide, is distilled with an excess of *sulphuric acid*, and a little *binoxide of manganese* in a small retort, to which a glass condenser has been adapted. If bromine be present brownish or yellowish-red vapors appear immediately on the application of heat, which impart an orange-yellow color to *starch-paste* in the receiver.

Pure bromides, when distilled with *chromate of potassa* and *concentrated sulphuric acid*, disengage only bromine, the color of which disappears on the addition of *ammonia* (distinction between chlorides and bromides and detection of the former in bromides).

Bromides, when heated before the blowpipe with a bead of *phosphorus-salt* saturated with *oxide of copper*, exhibit the same comportment as chlorides, the color of the flame is however rather *greenish*.

HYDRIODIC ACID.

HI.

Hydriodic acid and iodides resemble very much in their behavior the corresponding chlorine and bromine compounds.

Nitrate of silver produces in solutions of iodides a yellowish-white precipitate of iodide of silver, Ag I, insoluble in nitric acid, but only slightly soluble in ammonia.

Subnitrate of mercury forms a yellowish-green precipitate of subiodide of mercury, Hg_2I.

Chloride of mercury throws down scarlet-red iodide of mercury, Hg I.

Subsalts of copper produce a dingy white precipitate of subiodide of copper, Cu_2I (a mixture of 1 part of *sulphate of copper*, and $2\frac{1}{2}$ parts of *sulphate of oxide of iron*, or a salt of *oxide of copper*, to which *sulphurous acid* has been added, has the same effect, as each contains a salt of *suboxide of copper*).

Lead salts precipitate orange-yellow *iodide of lead*, Pb I.

Bismuth salts throw down brown iodide of bismuth.

Salts of oxide of palladium produce a black precipitate of iodide of palladium, even in very highly dilute solutions of iodides.

With *chlorine*, with *concentrated sulphuric acid* and *binoxide of manganese*, and with *nitric acid*, iodides exhibit a behavior similar to that of bromides; iodine is separated, which according to its amount is precipitated as a black powder or remains in solution, imparting a brown color to the liquid. On heating this liquid the characteristic violet vapors of iodine are obtained.

On bringing iodine, separated from any compound, into contact with *starch-paste*, a blue combination is produced, which may appear violet or rose-red, if iodine exists in very minute quantities. For this purpose dilute starch-paste is mixed with the liquid to be examined for an iodide, and then *chlorine water*, *nitric acid*, or *sulphuric acid*, carefully added to liberate the iodine. On adding too large an amount of chlorine-water to the solution, chloride of iodine is produced, which prevents the formation of the blue compound,

the same production takes place by nitric acid in the presence of a considerable amount of chlorides.

From dry compounds iodine is separated by sulphuric acid in a flask with a ground stopper; a strip of paper moistened with starch-paste is then fixed between the neck and the stopper. If iodine be present, this paper will assume a blue color after a few hours.

Iodides, when heated before the blowpipe with a bead of *phosphorus salt* saturated with *oxide of copper*, impart a fine *green* color to the flame.

HYDROFLUORIC ACID.

HF.

Hydrofluoric acid is a very volatile liquid, giving off very pungent and acid fumes when in contact with the air, and having a very powerful and injurious effect upon the respiratory organs. This acid mixes with water, producing considerable heat.

Some of the fluorides are soluble, as the alkaline fluorides, fluoride of silver and fluoride of tin; some are slightly soluble or insoluble, as fluoride of lead, fluoride of cadmium, fluoride of zinc, and the compounds of fluorine with the metals of the alkaline earths.

Lime water produces in soluble fluorides, an almost transparent gelatinous precipitate of fluoride of calcium, Ca F, which becomes visible by addition of *ammonia*, and dissolves but with difficulty in hydrochloric acid or nitric acid.

Nitrate of silver does not precipitate solutions of fluorides.

All the fluorides are decomposed by *boiling concentrated sulphuric acid* with disengagement of hydrofluoric acid. If nascent hydrofluoric acid meets with *silicic acid* (ex. gr., in glass) these two compounds decompose each other, water and fluoride of silicon being formed.

$$Si\ O_2 + 2\,HF = Si\ F_2 + 2\,HO.$$
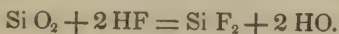
On this property depends the test for fluorine by its action on glass.

If the compound to be examined contains silicic acid, sulphuric acid disengages, instead of hydrofluoric acid, fluoride of silicon, which does not attack glass, but decomposes water with separation of gelatinous silicic acid, and formation of hydrofluosilicic acid.

$$3\ Si\ F_2 + 2\ HO = Si\ O_2 + 2\ (HF, Si\ F_2).$$
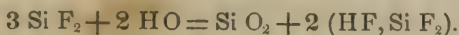
This reaction may be employed for ascertaining the presence of fluorine in silicates. For this purpose the compound under examination is finely powdered and heated with concentrated sulphuric acid in a small glass flask well dried; on passing the fluoride of silicon, which is disengaged, through a glass tube, moistened inside, the inner surface becomes coated with a white deposit of silicic acid. In testing compounds which do not contain silicic acid, for fluorine, by this method, a little powdered glass or quartz is added, before they are heated with sulphuric acid.

Insoluble fluorides are decomposed by fusion with *alkaline carbonates*, a soluble alkaline fluoride being formed. On neutralising the solution of the fused mass carefully with hydrochloric acid, and adding *chloride of calcium* and *ammonia*, all the fluorine is precipitated

in the form of fluoride of calcium. If phosphoric acid
be present in the compound, the precipitate contains
phosphate of lime in admixture.

On heating a fluoride by the blowpipe in a glass
tube, open at both ends, the glass around the fluoride
is attacked. If a mixture of a fluoride with *bisulphate
of potassa* is heated in a test-tube, hydrofluoric acid is
disengaged, which is easily detected by the roughening
of the glass.

HYDROCYANIC ACID. PRUSSIC ACID.

H Cy.

Anhydrous hydrocyanic acid is a colorless very
volatile liquid, which burns with a weak flame. It
possesses a peculiar suffocating odor. Hydrocyanic
acid mixes in every proportion with water, alcohol and
ether; the dilute solution in water has the taste of
bitter almonds. When completely pure, it is gradually
transformed into a brownish-black mass and ammonia.
In the presence of concentrated mineral acids, it de-
composes with the elements of water, formic acid and
ammonia being formed.

$$C_2N\,H + 4\,HO = HO,\,C_2H\,O_3 + NH_3\,.$$

Hydrocyanic acid.   Formic acid.   Ammonia.
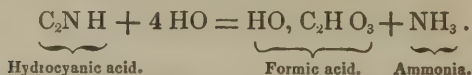
The compounds of cyanogen, with the metals of the
alkalies and of the alkaline earths, are soluble in
water; these solutions have an alkaline reaction, and
are decomposed by the weakest acids with separation
of hydrocyanic acid. On boiling the solutions with an
excess of alkali, ammonia and formic acid are pro-

duced. Cyanide of potassium and cyanide of sodium, when protected from the air, may be heated to redness without decomposition. In the presence of air, or of metallic oxides, cyanates are produced.

The other cyanides (with the exception of a few, as cyanide of mercury) are insoluble in water; by the action of heat some of them are separated into metal and cyanogen (cyanide of mercury), some of them are converted into inferior cyanides with disengagement of cyanogen (cyanide of silver), others into para-cyanides or into carbides (carburets) with disengagement of nitrogen. Most compounds of cyanogen with heavy, and especially with the precious metals, are not decomposed by dilute oxygen acids; all, however, are decomposed by hydrochloric and hydrosulphuric acids, with disengagement of hydrocyanic acid.

Nitrate of silver precipitates from solutions of hydrocyanic acid and cyanides white curdy cyanide of silver, Ag Cy, which is insoluble in dilute nitric acid, but dissolves in concentrated nitric acid, in ammonia, and cyanide of potassium. When moistened with concentrated hydrochloric acid, this precipitate of cyanide of silver disengages hydrocyanic acid.

Subnitrate of mercury throws down a grey precipitate of reduced mercury in solutions of hydrocyanic acid, cyanide of mercury remaining in solution.

$$H Cy + Hg_2 O = Hg Cy + Hg + HO.$$
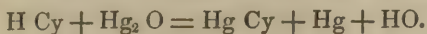
Sulphate of copper, to which sulphurous acid has been added, precipitates white subcyanide of copper.

Hydrocyanic acid dissolves *oxide of mercury*, cyanide of mercury being formed, which is not precipitated

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by the alkalies; if hydrochloric acid be present at the same time, *ammonia* produces a precipitate of the double compound of chloride and amidide of mercury.

On adding to a solution containing hydrocyanic acid, *potassa* and a mixture of *salts of oxide and sesquioxide of iron* (a solution of the *sulphate of the oxide*, which has been partly oxidised in the air, is generally employed), a dingy greenish-blue precipitate is produced, which, after addition of sufficient hydrochloric acid, assumes the pure blue color of prussian blue, the oxide and sesquioxide of iron, which has been precipitated along with it, being dissolved by the acid.

The cyanides of the metals form with the alkaline cyanides double compounds, most of which are soluble in water and undecomposable by alkalies.

The cyanides of iron, cobalt, manganese, and chromium, when meeting with alkaline cyanides, unite with their cyanogen into peculiar salt-radicals, in which the presence of the heavy metal cannot be ascertained in the ordinary way, not even by *sulphide of ammonium*. The alkaline salts of these compound radicals are decomposed by dilute sulphuric acid, with disengagement of hydrocyanic acid, and by concentrated sulphuric acid with evolution of carbonic oxide. When ignited alone, or with an alkaline carbonate, they are converted into soluble cyanides with separation of the metal.

In the moist way ferrocyanides and ferricyanides are recognised by their behavior with iron and copper-salts, (v. pp. 25, 26, and 39.)

HYDROSULPHOCYANIC ACID.

$$H \, Cy \, S_2.$$
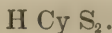
The compounds of hydrosulphocyanic acid with the alkalies and alkaline earths, are soluble in water, most sulphocyanides of the metals are insoluble.

The alkaline sulphocyanides out of contact with the air may be heated to redness without decomposition; in contact with oxygen, however, they are converted into cyanates and sulphates, with disengagement of sulphurous acid. The sulphocyanides of the heavy metals are decomposed by heat, at first sulphide of carbon and sulphur, and on raising the temperature a mixture of nitrogen and cyanogen being disengaged.

Hydrosulphocyanic acid, when separated from its compounds by mineral acids, forms a colorless liquid, which, however, in contact with air or on application of heat, is easily decomposed into a variety of products, amongst which invariably a lemon-yellow powder appears.

Salts of sesquioxide of iron impart to soluble sulphocyanides a deep blood-red color, which affords a very characteristic reaction for these salts.

OXYGEN ACIDS OF THE SALT-RADICALS.

[PERCHLORIC ACID.]

$$HO, \, Cl \, O_7.$$

Perchlorates are soluble in water; the potassa salt is rather difficultly soluble. Their solutions do not destroy vegetable colors, and are not decomposed either

by acids, or reducing agents; neither sulphuric acid nor hydrochloric acid imparts a yellow color to their solutions. When ignited they exhibit the same behavior as chlorates.

CHLORIC ACID.

HO, Cl O$_5$.
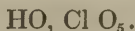
All chlorates are soluble in water; their solutions do not possess bleaching properties; they are however decomposed by sulphuric acid, with formation of perchloric acid, chlorine, hypochloric acid and oxygen being set free, which impart a yellow or brownish color to the liquid.

When mixed with *sulphuric acid* they destroy the color of *litmus* in the cold, and decolor *sulphindigotic acid* on application of heat.

All chlorates are decomposed by heat, with evolution of oxygen; the alkaline chlorates in this process leave pure chlorides; most of the other chlorates give a residue of oxide, a mixture of oxygen and chlorine being disengaged.

Chlorates deflagrate violently, when heated with combustible bodies, as carbon, sulphur, phosphorus, cyanides, etc.

HYPOCHLOROUS ACID.

Cl O.

Hypochlorites as far as they are known are soluble in water; they possess an astringent pungent taste and evolve the odor of chlorine; they are decomposed when heated by themselves or when exposed to light, most

of them with evolution of oxygen, a mixture of chlorate and chloride remaining.

Hypochlorites destroy vegetable colors especially on addition of an acid.

They are decomposed by *acids*, only chlorine being evolved.

Hypochlorites are powerful oxidising agents.

They precipitate from *salts of oxide of manganese* brownish-black hydrate of binoxide of manganese.

In *lead salts* they produce at first a white precipitate of chloride of lead, and then of brown binoxide of lead.

BROMIC ACID.

HO, Br O$_5$.

Most bromates are soluble in water; when heated alone, or with combustible bodies, they exhibit the same behavior as chlorates.

They are decomposed by *oxygen acids*, with disengagement of oxygen and bromine.

By the action of *hydrochloric acid* they are converted into chlorides, with formation of chloride of bromine.

Hydrosulphuric acid reduces bromates to bromides, with separation of sulphur and formation of sulphuric acid.

Sulphurous acid, when meeting with bromates, is converted into sulphuric acid, bromine being set free.

Subsalts of mercury produce in bromates a light-yellow precipitate soluble in nitric acid.

Nitrate of silver throws down a white bromate of silver, which is readily soluble in ammonia, but dissolves only with difficulty in dilute nitric acid.

[PERIODIC ACID.]

HO, IO_7.
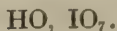
Most periodates are difficultly soluble in water, easily soluble in nitric acid.

The silver salt is light-yellow, and becomes blackish-red, when heated with water.

IODIC ACID.

HO, IO_5.
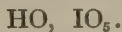
Most iodates are insoluble or difficultly soluble in water; only the neutral alkaline iodates are easily soluble.

In solutions of iodates *lead salts* produce a white precipitate of iodate of lead.

Silver salts throw down a white precipitate of iodate of silver, which is soluble in ammonia, but dissolves only with difficulty in nitric acid.

When heated, iodates and periodates exhibit the same comportment as chlorates.

Iodates are decomposed by *chloride of tin* and *sulphurous acid*, with separation of iodine, binoxide of tin and sulphuric acid being formed. On adding some *starchpaste* in this reaction, the characteristic blue compound is formed.

Hydrosulphuric acid decomposes iodates, with separation of sulphur, water, sulphuric acid and an iodide being formed.

CYANIC ACID.

HO, Cy O.
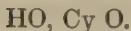
Most cyanates are soluble in water. They are de-
composed by strong mineral acids, with effervescence,
carbonic acid being disengaged, with a pungent odor
from an admixture of undecomposed cyanic acid; after
this decomposition, the liquid contains ammoniacal salt.

$$KO,C_2NO+2HO,SO_3+2HO=2CO_2+NH_4O,SO_3+KO,SO_3.$$
<u>Cyanate of potassa.</u>   Carbonic acid.

The alkaline cyanates are not decomposed by
ignition.

ACIDS OF BORON, SILICON AND CARBON.

BORACIC ACID.

Bo O₃.

This acid crystallises from the watery solution in
scales containing water; these crystals, when ignited,
fuse to an anhydrous glassy mass. When alone,
boracid acid is completely fixed; when, however, an
aqueous or alcoholic solution is evaporated, it is partly
volatilised with the vapors of the solvent.

The alkaline borates are readily soluble in water,
the other salts are difficultly soluble, none insoluble;
the latter are easily soluble in acids and ammoniacal
salts.

From moderately dilute solutions of borates, mineral
acids separate boracic acid, which crystallises in scales.

On heating a borate with concentrated *sulphuric
acid* and *alcohol*, and kindling the latter, the boracic

acid volatilising with the vapor, imparts a fine *green* color to the flame.

The blowpipe flame assumes the same *green* color, when a mixture of a borate and *bisulphate of potassa* is heated on the platinum wire.

On heating, most borates swell up and fuse into transparent glass, in which various oxides are soluble with various colors.

SILICIC ACID.

$$Si O_2.$$

Silicic acid occurs in nature both in a crystalline and in an amorphous state; when artificially prepared, it is always amorphous, forming a white tasteless powder, which, when boiled with caustic alkalies and their carbonates, dissolves far more easily than even the finest powder of crystalline silicic acid.

Silicic acid unites with bases in a great many proportions; all silicates, with the exception of some alkaline silicates, are insoluble in water. Many silicates may be decomposed by acids, such as those in which an alkaline base predominates, or those which contain water (zeolites). The form of the silicic acid separated, varies according to the nature of the silicate, and strength and quantity of the acid added. On saturating a dilute aqueous solution of an alkaline silicate with hydrochloric acid, no decomposition can be observed, the soluble modification of silicic acid remaining dissolved. On evaporating, however, this solution to a certain point, or on decomposing a rather concentrated solution of an alkaline silicate, silicic acid

separates either as a flaky powder, or as a gelatinous mass, which, when dried, forms a white impalpable powder, insoluble in all acids except hydrofluoric acid, the soluble modification having been converted into the insoluble.

Another class of silicates, when treated with acids, are only partially or not at all decomposed. The decomposition of these silicates may, however, be effected by fusing them with 3 or 4 times their amount of a *fixed caustic* or *carbonated alkali ;* in this case a silicate with predominating alkaline base is produced, which contains silicic acid in the soluble form.

If a silicate is to be tested for the alkalies (potassa, soda and [lithia]) the decomposition is to be effected by *hydrate of baryta.*

All silicates are completely decomposed by *hydrofluoric acid,* or what is equally good, by a mixture of *fluoride of calcium* (fluor spar) and *concentrated sulphuric acid.* The silicic acid, in this process, is disengaged as fluoride of silicon.

Dilute solutions of alkaline silicates nearly neutralised by mineral acids (nitric acid) are precipitated by most *heavy oxides,* by the *salts of the alkaline earths* and *ammonia.* This behavior involves the necessity of separating silicic acid, when investigating for the bases, by evaporating the hydrochloric acid solution to dryness, which converts the soluble modification into the insoluble. On digesting the dry mass with acid, all the basic oxides are dissolved, insoluble silicic acid remaining behind.

Pure amorphous silicic acid dissolves completely,

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when boiled with an aqueous solution of fixed caustic or carbonated alkalies.

When heated before the blowpipe with *carbonate of soda* (this salt should be employed in very minute quantity) silicic acid yields a colorless transparent glass, carbonic acid being set free with effervescence.

Fused *phosphorus-salt* dissolves only small quantities of silicic acid: the greater part swims in the red-hot bead as a swelled up mass; the glass obtained in this manner with pure silicic acid is always colorless, but according to the quantity in which it is present, more or less opaque. With small quantities, a transparent glass also in this way may be obtained. This behavior allows us to ascertain the presence of silicic acid before the blowpipe with facility.

[Titanic and tantalic acid,] which exhibit a behavior similar to that of silicic acid, are separated from the latter by means of *hydrofluoric acid*, which does not volatilise the former. A mixture of titanic and silicic acid may be separated by fusing with an alkaline carbonate, exhausting the mass first with *water*, and treating the residue with cold concentrated *hydrochloric acid*. *Ammonia* precipitates from this hydrochloric acid solution a mixture of silicic and titanic acid, from which, after drying, only titanic acid is dissolved by strong hydrochloric acid.

CARBONIC ACID.

CO_2.

At the common atmospheric pressure, carbonic acid is a colorless transparent gas, not inflammable, and possessing a feebly acid odor. The specific gravity of

this gas is nearly 1.5, air $=1$, and it may therefore be poured from one vessel into another.

All neutral carbonates, the alkaline excepted, are insoluble in water. They are all decomposed by strong mineral acids, with evolution of carbonic acid. The carbonates insoluble in water dissolve when a sufficient quantity of free carbonic acid is present in the form of bicarbonates. These solutions are reprecipitated by boiling, the excess of carbonic acid being expelled.

When brought together with *lime* and *baryta-water*, carbonic acid gas or its aqueous solution forms a white precipitate of carbonate of lime or carbonate of baryta, which is soluble in hydrochloric acid, with effervescence.

When ignited, carbonates lose their carbonic acid, with the exception of the carbonates of the alkalies and some alkaline earths (baryta, strontia).

ORGANIC ACIDS.

The greater number of organic acids cannot be safely distinguished qualitatively; a smaller number, however, embracing just those occurring most frequently, may be qualitatively recognised.

These are the following: —

Oxalic acid.	[Quinic acid.]
Tartaric acid.	[Meconic acid.]
[Racemic acid.]	Gallic acid.
Citric acid.	Tannic acid.
[Malic acid.]	Uric acid.
Succinic acid.	Acetic acid.
Benzoic acid.	Formic acid.

The ten former of these acids are not volatile without decomposition, the latter four may be sublimed or distilled undecomposed.

The compounds of all these acids with the alkalies and the alkaline earths, when ignited with exclusion of the atmosphere, are converted into carbonates with separation of carbon, oxalates only excepted, which are not blackened by ignition.

The non-volatile organic acids are blackened when heated with concentrated sulphuric acid, carbonic acid, carbonic oxide and sulphurous acid being disengaged. Oxalic acid forms an exception even here, this acid being decomposed by sulphuric acid into carbonic acid and carbonic oxide, without separation of carbon.

The following are the characteristic reactions of these acids.

a. OXALIC ACID.

$$HO, C_2 O_3 = HO, \overline{O}.$$
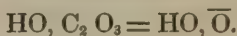
Oxalates soluble in water produce with *lime-water*, or soluble *lime-salts*, even with *sulphate of lime*, a white precipitate of oxalate of lime, which is insoluble in acetic acid, but dissolves readily in hydrochloric and nitric acids. Oxalates insoluble in water and dissolved in acids produce the same precipitate after a sufficient quantity of *acetate of ammonia* has been added.

b. TARTARIC ACID.

$$2 HO, C_8 H_4 O_{10} = 2 HO, \overline{T}.$$

Tartaric acid and tartrates, when heated, evolve a very peculiar odor. An aqueous solution of tartaric

acid and a tartrate is precipitated by an excess of *lime-water*.

In solutions of the tartrates *chloride of calcium* produces the same precipitate, which dissolves readily in ammoniacal salts and cold potassa.

The solution of this precipitate in potassa forms a gelatinous mass on boiling, which disappears again on cooling.

[c. RACEMIC ACID.]

$$HO, C_4 H_2 O_5 = HO, \overline{R}.$$
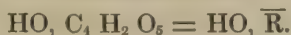
Racemic acid (paratartaric acid) is distinguished from tartaric acid by the insolubility of its lime-salt in ammoniacal salts, and in an excess of racemic and tartaric acids.

d. CITRIC ACID.

$$3 HO, C_{12} H_5 O_{11} = 3 HO, \overline{Ci}.$$
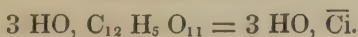
Lime-salts do not precipitate an aqueous solution of citric acid or citrates *in the cold ;* on boiling, however, a white precipitate of citrate of lime is obtained, if the liquid be neutral, or if it contain an excess of lime-water or free ammonia. This precipitate is insoluble in potassa, but soluble both in ammoniacal salts and free acids.

[e. MALIC ACID.]

$$2 HO, C_8 H_4 O_8 = 2 HO, \overline{M}.$$

When heated in a test-tube malic acid is decomposed, with formation of a crystalline sublimate of malic acid, fumaric acid remaining behind.

Acetate of lead produces in aqueous solutions of malic acid, or malates, a white precipitate of malate of lead, which when remaining in the liquid for some time becomes crystalline. This precipitate, if not mixed with another insoluble salt, fuses into a transparent mass, if the liquid be boiled.

Lime-water does not precipitate malic acid, either in the cold or on boiling.

[*f*. QUINIC ACID.]

$$2 \text{ HO}, \text{ C}_7 \text{ H}_4 \text{ O}_4 = 2 \text{ HO}, \overline{\text{Qui}}.$$
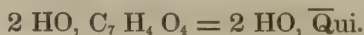
Even very small quantities of this acid may be detected by transforming it into quinone. For this purpose the liquid under examination, concentrated by evaporation, is distilled with half its weight of *sulphuric acid* and *binoxide of manganese*. If quinic acid be present, the first portion of the distillate is yellow (shooting into yellow crystals, if a large amount of acid is used), which assumes a blackish-brown color on being mixed with *ammonia*. *Chlorine water* renders it light-green.

[*g*. MECONIC ACID.]

$$3 \text{ HO}, \text{ C}_{14} \text{ HO}_{11} = 3 \text{ HO}, \overline{\text{Me}}.$$

Salts of sesquioxide of iron impart to solutions of meconic acid or meconates a blood-red color.

Hydrochloric acid precipitates from meconates meconic acid in very slightly soluble crystals, shining like mother o' pearl.

Meconic acid is decomposed by *potassa* into oxalic acid, carbonic acid and a dark reddish-brown substance.

h. TANNIC ACID.

$$HO, C_{18} H_5 O_9 = HO, \overline{Qt}.$$

This acid is precipitated by *mineral acids*, in the form of a paste. It is thrown down also by *dilute starch-paste*, by *gelatine* and *albumen*.

Tannic acid may be completely withdrawn from its solution by placing into it a piece of *animal membrane*.

Salts of sesquioxide of iron produce in solutions of tannic acid, or tannates, a dark blackish-blue precipitate.

The same effect is produced by *salts of oxide of iron*, but only on exposing the mixture to the air.

i. GALLIC ACID.

$$2 HO, C_7 H O_3 = 2 H O, \overline{G}.$$
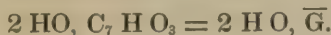
The solutions of this acid are *not* precipitated by solutions of *gelatine* or by *animal membrane*. By this behavior it may be distinguished and separated from tannic acid.

An *alkaline* solution of gallic acid, when exposed to the air, assumes successively a yellow, green, red, and at last a brownish-black color.

Salts of sesquioxide of iron produce a dark-blue precipitate in solutions of gallic acid.

With *salts of oxide of iron* the precipitate is black.

k. URIC ACID.

$$HO, C_5 H N_2 O_2 = H O, \overline{U}.$$

Mineral acids separate uric acid from its compounds in form of a white crystalline powder.

On dissolving uric acid in *nitric acid*, evaporating nearly to dryness and saturating with *ammonia*, a beautiful purple-red color is obtained.

On fusion with *alkalies* uric acid disengages ammonia, the residue, if not too powerfully heated, containing a mixture of cyanide of potassium and cyanate of potassa.

l. SUCCINIC ACID.

$$HO, C_4 H_2 O_3 = HO, \overline{S}.$$

Almost all the salts of this acid are soluble in water.

Salts of sesquioxide of iron produce in neutral solutions a brownish-red voluminous precipitate, which is readily soluble in acids. *Ammonia* renders it darker, a quantity of succinic acid being withdrawn.

Solutions of succinic acid, after addition of alcohol and ammonia, are precipitated also by *chloride of barium*.

m. BENZOIC ACID.

$$HO, C_{14} H_5 O_3 = HO, Bz O = HO, \overline{Be}.$$

Benzoic acid is very slightly soluble in cold water, being less so than succinic acid; it is therefore precipitated in the form of a white crystalline powder on decomposing its salts by hydrochloric acid.

With *sesquichloride of iron* it exhibits the same behavior as succinic acid; the precipitate, however, is not brownish-red, but pale-yellow. Both acids on being heated evolve vapors, which, irritating the air-passages, produce coughing.

n. ACETIC ACID.

$$HO, C_4 H_3 O_3 = HO, Ac O_3 = HO, \overline{A}.$$

All the salts of acetic acid are soluble in water; only the silver and mercury salts are but slightly soluble. Most acetates when heated evolve acetone, which is inflammable and possesses a very characteristic odor.

$$\underbrace{KO, C_4 H_3 O_3}_{\text{Acetate of potassa.}} = KO, CO_2 + \underbrace{C_3 H_3 O.}_{\text{Acetone.}}$$
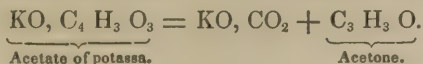
Salts of sesquioxide of iron impart to solutions of acetates a blood-red color.

When heated with a mixture of *sulphuric acid* and *alcohol*, acetates disengage acetic ether, easily distinguished by its characteristic odor.

A solution of free acetic acid, when digested with an excess of *oxide of lead*, yields an alkaline solution, a property which formic acid does not possess.

Acetates when heated with *potassa* and *arsenious acid*, disengage oxide of kakodyl (v. p. 57).

o. FORMIC ACID.

$$HO, C_2H O_3 = HO, Fo O_3 = HO, \overline{F}.$$
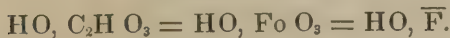
Formic acid and formiates may be recognised by their possessing the property of reducing the oxides of the precious metals, with evolution of carbonic acid. For this purpose the solution to be examined for formic acid is heated with *nitrate of silver, subnitrate of mercury* or finely powdered *oxide of mercury.* Formic acid by this process is completely destroyed.

$$HO, C_2 H O_3 + 2 HgO = 2 Hg + 2 CO_2 + 2 HO.$$
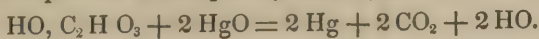
Acetic acid subjected to the same treatment is not decomposed.

On gently heating *chloride of mercury* with formiates, subchloride of mercury is first precipitated and afterwards reduced to metallic mercury.

Concentrated sulphuric acid decomposes formic acid, and formiates, with evolution of pure carbonic oxide.

$$HO, C_2 H O_3 + HO, SO_3 = 2 CO + HO, SO_3 + 2 HO.$$
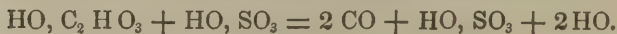
SECTION III.

COURSE OF QUALITATIVE ANALYSIS.

I.—PRELIMINARY EXAMINATION OF SOLIDS.

SOLUTION.

BEFORE subjecting a solid substance to qualitative analysis, its physical properties should be carefully observed. The form, color, lustre, specific gravity, &c. of bodies in many cases, may indicate much with respect to their composition.

The proper qualitative analysis, moreover, should always be preceded by an examination in the dry way, comprising the comportment of the substance at a high temperature, with access of air, and with exclusion of air, alone, and in presence of some reagents, which effect either simple solution, or chemical decomposition.

This preliminary examination embraces only the following few experiments, from the results of which however many definite conclusions may often be drawn, especially after some experience.

1. The substance is to be heated on platinum-foil (in a small iron spoon or a porcelain dish), and in a dry test-tube over the spirit-lamp.

2. It is to be ignited by the blowpipe flame in a glass tube, open at both ends, held obliquely.

3. The substance is acted on upon charcoal with the different flames of the blowpipe, either *alone* or with *carbonate of soda*, or with a mixture of *carbonate of soda* and *cyanide of potassium;* or it is heated with *phosphorus-salt* or *borax* on platinum-wire.

4. The substance is heated in a test-tube with *concentrated sulphuric acid.*

5. Successive treatment of the finely-powdered substance with different solvents, viz., *water*, *hydrochloric acid*, *nitric acid*, and *nitro-hydrochloric acid.*

6. Substances, which are insoluble in the above-mentioned solvents, are to be heated with from three to four times their weight of *carbonate of soda*, with *hydrate of baryta*, with *bisulphate of potassa*, with a mixture of *nitre* and *carbonate of soda*, or in an atmosphere of *chlorine.*

In making these preliminary experiments, only a small portion of the substance under examination is employed. From the results obtained, the process is to be inferred to which the greater part of the substance must be subjected, in order to obtain it in solution.

By the first experiment (heating the substance on platinum-foil and in a test-tube) we ascertain, whether it is wholly or partially volatile or not volatile, whether it fuses, changes color, or decomposes into other products; whether the solid, or its volatile constituents,

are combustible, and whether these latter escape as permanent gases or condense into a liquid distillate, or a solid sublimate, &c.

Most minerals, and a great number of chemical compounds, disengage water, which condenses on the colder part of the test-tube into droplets or a thin film.

This water must always be examined by test-papers for an acid or alkaline reaction.

Salts of ammonia and mercury compounds are completely volatile, some with decomposition, others undecomposed; this property belongs also to some sulphides, selenides, and oxides, ex. gr., those of arsenic.

If a solid substance blackens on heating (separation of charcoal) the presence of organic matter is almost certain.   Oxalates only are decomposed without blackening.   All organic matter disappears completely when ignited continuously in contact with the atmosphere.   Compounds of organic acids with alkalies or alkaline earths leave, after ignition, carbonates, which may be recognised by treating the ignited residue with acids, the absence of carbonic acid in the substance to be examined having been previously ascertained.   The compounds of organic acids with other oxides leave either pure oxides or reduced metal. When organic substances are present, the examination for non-volatile inorganic constituents is greatly facilitated by igniting them in a porcelain, or platinum * crucible in contact with the air.

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* If compounds of metals, and especially of those metals which are easily reducible, and fusible, as lead, arsenic antimony, tin,

Some metallic oxides when ignited assume another (in most cases darker) color than they possess at common temperatures. Oxide of zinc, binoxide of tin [titanic acid] become yellow; oxide of lead, teroxide of bismuth, and oxide of mercury far darker, almost black.

Many compounds of inorganic acids, with the alkalies and with alkaline earths, (nitrates, chlorides, &c.,) fuse on ignition; salts containing water of crystallisation lose this water on ignition, some of them with intumescence (borates), others with decrepitation (chloride of sodium, &c.).

A great many salts lose, with their water, part of or all their acid, either decomposed, or undecomposed, ex. gr., the compounds of heavy oxides, and alkaline earths, with carbonic acid, sulphuric acid, nitric acid, chloric acid, bromic acid, iodic acid. The last three, also, when combined with alkalies, are destroyed by heat.

On heating a substance in a tube open at both ends, the presence of sulphides is easily ascertained (formation of sulphurous acid) also [selenides] and compounds of arsenic may be recognised in this way. If in this treatment a white infusible sublimate is formed, the presence of arsenious acid or teroxide of antimony is very probable. [Tellurous acid] and teroxide of bismuth

&c., are present in the substance under examination, the use of platinum crucibles is always to be avoided, for easily fusible alloys of platinum with these metals form, and destroy the crucibles.

also form white sublimates, which, however, fuse on heating, the former into colorless, the latter into brown or yellow drops.

Many sulphides (sulphides of mercury and arsenic) volatilise without decomposition, and also the combinations of mercury with chlorine, all other compounds of this metal yielding a grey incrustation, which by rubbing, forms metallic globules. Fluorides are easily recognised by their action on glass, when heated together with *phosphorus-salt* or *bisulphate of potassa.*

If a saline substance fuses, when heated on charcoal before the blowpipe, the presence of alkalies is very probable. From a white infusible residue it may be inferred that alkaline earths are present. Alkaline salts, in this case, either fuse into the charcoal or form beads. A great many metals and sulphides are fusible in the blowpipe-flame, most oxides are infusible; the earths, especially lime [and zirconia] become very luminous in the blowpipe-flame. On moistening a white infusible residue obtained in this way on the charcoal with *cobalt-solution*, and igniting again strongly, from the production of a green color, oxide of zinc, from a flesh-red color, magnesia, and from a blue color, alumina may be inferred; the color, although less intense, appears, however, also with many phosphates and silicic acid.

Nitrates, [perchlorates,] chlorates, bromates and iodates deflagrate on ignited charcoal.

Gold, silver, copper and tin compounds, when

heated with a mixture of *carbonate of soda* and *cyanide of potassium* in the inner flame of the blowpipe, yield metallic beads, but no incrustations; iron, nickel, cobalt, platinum, [tungsten and molybdenum] compounds give neither beads, nor incrustations; bismuth, lead and cadmium compounds produce a yellow or brown deposit on the charcoal; antimony, zinc [and tellurium] give a white incrustation; arsenic may easily be recognised by its odor.

The salts of alkalies, when heated with *carbonate of soda*, fuse into the charcoal; the earths remain as an infusible mass. Silicic acid on charcoal, as well as on platinum-wire, fuses with *carbonate of soda* into a transparent glass. Titanic acid forms an opaque greyish-white glass.

Compounds of manganese, when heated with *carbonate of soda* in the oxidising flame of the blowpipe, produce a bluish-green mass (manganate of soda).

If after fusion with *carbonate of soda* in the inner flame of the blowpipe a brown residue is obtained, which when moistened with water produces a black spot on silver foil, and disengages hydrosulphuric acid when drenched with an acid, sulphur is present, either in form of a sulphide, or as a salt of an oxygen acid of sulphur.

Almost all oxides fuse into transparent glasses, either colorless or colored, when heated with *phosphorus-salt* on platinum-wire before the blowpipe.

The color of the glasses obtained in this manner, may vary according to the flame in which they are produced.

The oxides of the alkali-metals, and of the

metals of the alkaline earths generally, produce colorless glasses, whilst glasses obtained with oxides yielding colored salts, are in general also colored. Silicic acid is insoluble or almost insoluble in *phosphorus-salt*, a reaction, by which this acid and its compounds may be easily distinguished.

On heating a solid substance with concentrated *sulphuric acid*, we ascertain at once, whether a volatile acid is present or not. In most cases, from the odor or color of the gas disengaged, or from the products of decomposition evolved, the nature of the acid may be inferred. Sulphides, by this treatment, give off hydrosulphuric acid mixed with sulphurous acid; all the inferior oxides of sulphur disengage sulphurous acid. Nitrates and nitrites, the former in presence of most metals (*copper*) evolve red fumes of nitrous acid. Chlorates disengage a yellow gas (chlorine and hypochloric acid); bromates a mixture of bromine and oxygen. Chlorides, with a few exceptions, give off hydrochloric acid; bromides and iodides, brown vapors of bromine, or violet clouds of iodine with a simultaneous disengagement of sulphurous acid. Fluorides evolve hydrofluoric acid, etching glass. Cyanides yield carbonic oxide, burning with a blue flame, or if the *sulphuric acid* be less concentrated, hydrocyanic acid. Oxalates, a mixture of carbonic acid and carbonic oxide; carbonates, pure carbonic acid. Most organic compounds are decomposed when heated with *strong sulphuric acid*, sulphurous acid, carbonic acid, and carbonic oxide being disengaged, which often ren-

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ders it difficult to recognise the presence of volatile acids. The salts of the acids not volatile and undecomposable by *sulphuric acid* (p h o s p h o r i c a c i d, a r s e n i c a c i d, b o r a c i c a c i d, s i l i c i c a c i d, and i o d i c a c i d), remain either undecomposed, or yield, at least, no volatile compounds.

After the preliminary investigation has pointed out to which class of compounds the substance under examination belongs, we now must bring it into that form, which is most fitted for analysis, *i. e.*, we must dissolve it. If a substance occurs in large pieces, or a coarse powder, we must first reduce it by mechanical means to as fine a powder as possible. In many cases it is necessary to levigate it; this applies to all minerals, especially to silicates, and in general to all compounds which are decomposed with difficulty.

It is now first to be tried, whether the substance is w h o l l y or p a r t l y soluble in *water* (in the latter case, a drop of the liquid, when evaporated on platinum foil, will leave a visible spot), and then the aqueous solution is to be examined, whether it is neutral, alkaline or acid. If a substance be only partly soluble in water, the constituents of the dissolved and of the undissolved portion are to be ascertained separately. If water does not dissolve anything, the action of *dilute* or *concentrated hydrochloric acid* is to be tried, and attention should be paid to the gases, which are disengaged in the process. From c a r b o n a t e s, *hydrochloric acid* expels carbonic acid with effervescence; p e r o x i d e s evolve chlorine; many s u l p h i d e s, hydrosulphuric acid; and some m e t a l s, hydrogen gas.

Hydrochloric acid either dissolves the substance c o m p l e t e l y, or a r e s i d u e remains, which is to be carefully separated from the liquid.

This residue, or a substance insoluble in *hydrochloric acid*, we now treat with *nitric* or *nitro-hydrochloric acid.* Many sulphides by treatment with nitric acid leave sulphur, which by continued action of the acid, collects into yellow drops, swimming in the liquid. From s e l e n i d e s, by the same process, selenium is separated in the form of a brown viscid mass. Sulphuric and selenic acids are formed simultaneously in this process. When l e a d is present, white sulphate of this metal is formed. S u l p h i d e o f m e r c u r y does not dissolve in *nitric acid,* but is easily decomposed by *nitro-hydrochloric* acid. Most metals dissolve in *nitric acid;* a n t i m o n y and t i n, when acted on by *nitric acid,* yield white oxides insoluble in an excess of the acid.

If the substance under examination be insoluble in *water, hydrochloric, nitric* or *nitro-hydrochloric acids,* it is either a s u l p h a t e (sulphate of baryta, of strontia, of lime, of oxide of lead), a c h l o r i d e, b r o m i d e, or i o d i d e (silver, lead), a s i l i c a t e [t i t a n a t e, t a n t a l a t e, t u n g s t a t e] or it is a f l u o r i d e. Some p h o s p h a t e s and a r s e n i a t e s and some o x i d e s (binoxide of tin, antimonic acid, sesquioxide of chromium, sesquioxide of iron) when previously ignited, are also insoluble or difficultly soluble in *nitro-hydrochloric acid.* By a few blowpipe experiments (with *carbonate of soda* on charcoal, with *phosphorus-salt* on platinum-wire) we ascertain at once, whether a r e d u c i b l e m e t a l, a s u l p h a t e

or s i l i c a t e is present. All compounds in soluble in acids are decomposed by fusion with *alkaline carbonates*, i. e., their constituents transpose in such a manner, that they now exist in a soluble state. The sulphates of the alkaline earths may partially be decomposed even by boiling with a solution of an *alkaline carbonate ;* in the hot filtered liquid sulphuric acid may be detected ; the powder insoluble in water containing the base in form of a carbonate. S u l p h a t e of l e a d, when digested with *sulphide of ammonium*, is converted into black sulphide of lead and sulphate of ammonia. S i l i c a t e s [t i t a n a t e s and t u n g - s t a t e s] are fused for some time with a mixture of *carbonate of potassa* and *carbonate of soda*, or if we have to test for alkalies with *hydrate of baryta ;* the fused mass is then treated with dilute hydrochloric acid, the mixture evaporated to dryness, and the residue insoluble in water examined for silicic [titanic and tungstic] acid, &c. All the other compounds are contained in the hydrochloric acid solution.

2. QUALITATIVE ANALYSIS OF THE SUBSTANCE IN SOLUTION.

After having succeeded in obtaining, according to one of the methods described, a solution of the body under examination, the question now is, what are the components of this solution ? The physical examination of a mineral, the preliminary examination of a solid in the dry way, its behavior with different solvents, generally indicate at once the presence of one or another compound. These hints however sometimes do not suffice, or the body may contain other com-

pounds besides those indicated by the preliminary examination; we must then preceed with the regular analysis in the moist way, *i. e.*, by bringing the solution together with different known compounds, which are called reagents. By the phenomena and changes obtained in this way, and dependent on the production of new compounds of known properties, the presence of any given constituent is inferred. Now it is evident at once, that the solution of the substance under examination cannot be mixed at random with the first reagent which presents itself, but that a certain series of trials must be made systematically. The basis of this system is the behavior of bodies, with g e n e r a l r e a g e n t s, which are always employed in order to separate the components of the solution into different groups, well known and defined, by which a further separation and distinction is very much facilitated.

General reagents are —

    a. For the oxides of the metals: —
        Hydrosulphuric acid.
        Sulphide of ammonium.
        Carbonate of ammonia.
        Ammonia, and
        Potassa.

    b. For the acids: —

        Chloride of barium.
        Chloride of calcium.
        Nitrate of silver.
        Sesquichloride of iron.

In the qualitative analysis of liquids (*i. e.*, of solutions which we have not prepared ourselves) it is necessary —

1. To try by evaporating a portion on platinum-foil, or in a porcelain dish, whether the liquid contains volatile, or non-volatile components. In the latter case, the residue left on evaporation is to be subjected to all the experiments which constitute the preliminary examination of a solid, except of course those relating merely to the solution of the substance.

2. To try by test-papers whether the liquid possesses a neutral, an acid, or an alkaline reaction.

These simple experiments should never be omitted, as from their results the presence of whole groups of bodies may be inferred; of course in a liquid, which leaves no residue by careful evaporation, violent ebullition having been avoided, we never search for fixed bases. A n e u t r a l solution generally contains only salts of the pure alkalies, and alkaline earths; the saline solutions of most other oxides possessing an acid reaction. The presence of a free alkali in a solution (especially in the absence of organic compounds) excludes all oxides i n s o l u b l e in alkaline liquids; and if this alkaline reaction is owing to carbonates of the fixed alkalies, the presence also of alkaline earths is impossible. (Exceptions are sesquioxide of iron, sesquioxide of chromium, etc., in presence of non-volatile organic substances, oxides soluble in cyanide of potassium and alkaline sulphides, cyanides, sulphides and some others.) Thus from the presence of certain oxides the absence of certain acids may be inferred. A solution, in which we have found oxide of silver or subox-

ide of mercury, is not to be examined for hydrochloric acid; in a solution containing sulphuric acid, we need not search for baryta, strontia or oxide of lead. A metal completely soluble in nitric acid cannot contain gold, tin, etc.

The solution of a solid obtained in one or the other way, is now divided into two parts, of which one is devoted to the detection of the bases, while the other is reserved for finding out the acids.

A. DETECTION OF THE BASES, OR ELECTROPOSITIVE BODIES.

The principal guide for detecting the bases is Table I., which exhibits their behavior with general reagents very perspicuously. A little reflection on the contents of this table will render easily intelligible the system to be followed; an example, however, will facilitate its apprehension to the student.

Let us suppose, that we have in solution s i x bases, one belonging to each of the six sections, t e r o x i d e of antimony, oxide of cadmium oxide of nickel, alumina, baryta and magnesia.

On adding an excess of *hydrosulphuric acid-water* or passing *hydrosulphuric acid-gas* through the a c i d u - l a t e d solution, till the liquid even after s h a k i n g possesses a strong odor of this reagent, a n t i m o n y and c a d m i u m are precipitated in the form of sul- phides. These sulphides are filtered off, washed and separated according to the direction given in Table II.

The a c i d solution filtered off from the precipitate obtained by hydrosulphuric acid is now first mixed

with some *chloride of ammonium*, then neutralised by *ammonia* (an excess of ammonia does no injury), and treated by *sulphide of ammonium* as long as a precipitate is produced.

This reagent in the example before us throws down s u l p h i d e o f n i c k e l a n d a l u m i n a, which are filtered off, washed and separated according to Table III.

To the liquid filtered off from the precipitate produced by sulphide of ammonium is now added *carbonate of ammonia*, and some *free ammonia;* a precipitate of c a r b o n a t e o f b a r y t a is thrown down, which is further examined, as pointed out below.

To a portion of the filtrate from the alkaline earths (baryta) *phosphate of soda*, now is added; the crystalline precipitate which is produced shows the presence of m a g n e s i a. The further examination of this precipitate, and the method for the detection of the f i x e d a l k a l i e s (potassa, soda, [lithia]) is pointed out below (p. 128). For a m m o n i a the original solution is to be tested. *

In the qualitative analysis of compound bodies several rules are strictly to be followed : —

1. T h e p r e c i p i t a t i o n b y g e n e r a l r e a g e n t s m u s t b e c o m p l e t e. The precipitant is to be added by degrees as long as a precipitate takes place.   In the

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* It is convenient after the precipitation of each group, to ascertain whether the filtrate still contains a member of the following groups. For this purpose a few drops of each filtrate are evaporated on platinum foil; if on igniting, there remains no distinct residue, the liquid is not to be tested further for fixed constituents.

case of *hydrosulphuric acid* complete precipitation is known by the liquid possessing a strong odor of this gas even after shaking. The application of a gentle heat in almost all cases promotes the complete separation of the insoluble compound produced. If from the result of the preliminary examination, the presence of arsenic (in the form of arsenic acid) is concluded, the acidulated solution before the addition of *hydrosulphuric acid* is boiled with *sulphurous acid*, which renders arsenic precipitable at once by hydrosulphuric acid. Some metals (platinum, iridium, rhodium), are only slowly thrown down by *hydrosulphuric acid ;* on digesting however the solution at a gentle heat during from twelve to twenty-four hours a complete precipitation takes place.

2. The precipitates of the several groups are to be separated completely from the members of the following groups still in solution. This is effected by washing with *water* (to which in certain cases small quantities of *sulphide of ammonium* are added) either on the filter (by filtration), or in the test-tube (by decantation).

The neglect of these precautions defeats the purpose of the whole analysis ; the members of the various groups become mixed, and in the different stages of the analysis, reactions are obtained belonging to the incompletely separated members of other groups, and the student thus becomes completely confounded.

3. The mineral acid used in acidulating the original solution (if not already sufficiently acid) is *hydrochloric acid* or *nitric acid.* Both are employed dilute, or, if concentrated, in such small quantities as not to prevent the

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formation of insoluble sulphides. Generally *hydro-chloric acid* is chosen, and then the following points are to be considered.

Hydrochloric acid precipitates c o m p l e t e l y two oxides (o x i d e o f s i l v e r, and s u b o x i d e o f m e r-c u r y); another oxide (oxide of lead) is parti-a l l y thrown down. On obtaining therefore a w h i t e precipitate by addition of hydrochloric acid to the original solution, the presence of one, or some of these oxides, may be inferred.   In this case a sufficient quantity of *hydrochloric acid* is added, and the precipitate examined according to Table II.:

"P r e c i p i t a t e p r o d u c e d b y h y d r o s u l-p h u r i c a c i d; p o r t i o n i n s o l u b l e i n s u l-p h i d e o f a m m o n i u m; p r e c i p i t a t e o b t a i n-e d b y h y d r o c h l o r i c a c i d."

The precipitate, which is now produced by *hydro-sulphuric acid* is of course not further examined for o x i d e o f s i l v e r and s u b o x i d e o f m e r c u r y; it must however be tested for l e a d, chloride of lead being slightly soluble. The same applies to the original solution containing already *hydrochloric acid.* If the original liquid has been acidulated by *nitric acid* instead of hydrochloric acid, a portion of the original solution is to be tested for s u b o x i d e and o x i d e o f m e r c u r y, in case the precipitate produced by hydro-sulphuric acid be not completely soluble in *concentrated nitric acid;* the nitric acid solution of the precipitate of course is also to be tested for o x i d e o f s i l v e r by means of *hydrochloric acid.*

If the original solution was alkaline, a precipitate obtained by *hydrochloric* or *nitric acid* may consist of

silicic acid, a metallic oxide soluble in alkalies, a metallic acid, or a sulphide, chloride, iodide, bromide, or cyanide.

4. A white milky cloudiness, or precipitate, which appears on addition of *hydrosulphuric acid* to the sufficiently acidulated solution, is owing to the separation of sulphur, and indicates sesquioxide of iron, a higher oxide of manganese, chromic acid (in this case the solution originally red or yellow turns green), chloric acid, bromic acid, iodic acid, sulphurous acid, or some other oxygen acid of sulphur, &c. Free chlorine and also hypochlorous acid cause a separation of sulphur. Which of these compounds has precipitated the sulphur is to be ascertained in the further examination. In case of the simultaneous precipitation of a sulphide, the separation of sulphur cannot be observed, and particular experiments must decide the state in which a constituent, found in the course of the analysis, was present in the original solution. In a solution, ex. gr., iron, has been precipitated by means of *sulphide of ammonium ;* we have now to ascertain whether the original solution contained sesquioxide, or oxide, or both. The same applies to various oxides, as the oxide of tin, antimony, and arsenic, which, by *hydrosulphuric acid*, are thrown down indeed in the form of sulphides, corresponding to the original oxides, but from the solution in *sulphide of ammonium* are always obtained in the form of the highest sulphides.

5. If in the systematic course of qualitative analysis we find by the reagents pointed out in the tables, that a substance contains one, or several members of one,

or different groups, we have now (and this applies especially to the beginner) to institute, with the original body as well as the constituents separated, a series of experiments, by which the results obtained may be controlled. These confirmatory experiments should never be omitted by the student; his intention being not only to make himself acquainted simply with the course of qualitative analysis, but to become familiar with the behavior of bodies under all circumstances. It is only by following exactly this important rule that the less experienced student protects himself from errors and deceptions, generally arising from want of knowledge of the behavior of bodies, or from not observing the conditions which insure the success of his experiment, *i. e.*, the exhibition of the phenomenon, which constitutes the proof of the presence of a compound. For this purpose we have given, in the first and second section of this outline, a full account of the behavior of bases and acids with reagents, from which the details of his confirmatory experiments may be obtained.

The qualitative analysis of a substance containing various bases, as may be inferred from the preceding remark as well as from the synoptical tables, consists in the examination of the different precipitates obtained by the general reagents successively employed, as has been explained.

We have, therefore, to examine first —

I. THE PRECIPITATE OBTAINED BY HYDROSULPHURIC ACID,

which, according to its behavior with *sulphide of ammonium*, is divided into,

a. A portion soluble in sulphide of ammonium, and

b. A portion insoluble in sulphide of ammonium.

The second examination embraces,

II. THE PRECIPITATE OBTAINED BY SULPHIDE OF AMMONIUM.

We have then, thirdly, to examine

III. THE PRECIPITATE OBTAINED BY CARBONATE OF AMMONIA

in the liquid filtered from the preceding precipitate. It contains the carbonates of the alkaline earths.

The fourth examination embraces,

IV. THE REMAINING SOLUTION,

containing magnesia and the alkalies.

I. PRECIPITATE OBTAINED BY HYDROSULPHURIC ACID.

If, on adding a few drops of *hydrosulphuric acid-water* to a small portion of the acidulated liquid, a precipitate is obtained, the whole liquid is treated with a stream of *hydrosulphuric acid gas*, the precipitate filtered from the liquid and washed. The precipitate, when still moist, is now digested with a sufficient quantity of *sulphide of ammonium*, containing an e x - c e s s   o f   s u l p h u r, and thrown on a filter, in order to separate the soluble portion, and washed.* The

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* This experiment should always first be made with a small quantity of the precipitate, in order to ascertain whether indeed a portion of the sulphides is insoluble in *sulphide of ammonium.* If *hydrochloric acid* produces a colored precipitate in the filtrate — a white

soluble, as well as the insoluble portion, are to be further examined according to Table II.

II. PRECIPITATE OBTAINED BY SULPHIDE OF AMMONIUM.

This precipitate, as may be seen from Table I., consists of s u l p h i d e s, o x i d e s, and s a l t s.

Most sulphides belonging to this group possess a black or at least a darkish color, as n i c k e l, c o b a l t, i r o n [u r a n i u m]; but s u l p h i d e o f m a n g a-n e s e is flesh-colored, and s u l p h i d e o f z i n c is white. Oxides and salts are colorless, with the exception of s e s q u i o x i d e o f c h r o m i u m, which is green; [white o x i d e o f c e r i u m, when in contact with the air, assumes a brownish color].

It is evident, that a completely white precipitate, obtained by *sulphide of ammonium*, ought not to be examined for those metals, the sulphides of which are black or of a darkish color; in a black precipitate, of course, all the others may be contained. The sulphides of this group are soluble in *hydrochloric acid*, with evolution of hydrosulphuric acid; (sulphide of nickel and cobalt, however, are only very difficultly decomposed by hydrochloric acid). If the precipitate, well washed, does not disengage hydrosulphuric acid, when treated with *hydrochloric acid*, it consists merely

precipitate being due only to the separation of sulphur — the whole quantity of the precipitate obtained by *hydrosulphuric acid* is to be treated by *sulphide of ammonium*. If the sulphides contain s u l-p h i d e o f c o p p e r, *sulphide of ammonium* generally dissolves a small quantity of this metal. If therefore we find copper in the insoluble part of the precipitate, *sulphide of potassium*, instead of *sulphide of ammonium,* should be employed for digestion.

of oxides and salts. The further examination is carried out according to Table III.

III. PRECIPITATE OBTAINED BY CARBONATE OF AMMMONIA.

The liquid filtered from the precipitate, obtained by *sulphide of ammonium*, is now mixed with *carbonate of ammonia* and *ammonia* and gently heated.* The precipitate obtained in this way may contain c a r b o - n a t e o f b a r y t a , s t r o n t i a a n d l i m e . It is filtered off, and dissolved in dilute *hydrochloric acid.* The solution now containing the chlorides of the metals of the alkaline earths is then to be tested with,

1. *Sulphate of lime.* A precipitate produced i m - m e d i a t e l y indicates the presence of b a r y t a ; a precipitate appearing only after some time, is a proof of s t r o n t i a . If a solution is not precipitated, it can contain o n l y l i m e .

2. If b a r y t a or s t r o n t i a is present, another portion of the hydrochloric acid solution is precipitated completely by *dilute sulphuric acid.* If on saturating the filtrate with *ammonia*, and adding *oxalate of ammonia*, a white precipitate takes place, the presence of l i m e is proved.

3. If b a r y t a is present, a third portion of the hydrochloric acid solution is evaporated to dryness, the residue digested with *strong alcohol*, and the solution kindled. A pure red color indicates s t r o n t i a .

Moreover, the presence of b a r y t a may be ascer-

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* The original solution itself may be employed for this purpose, if *hydrosulphuric* acid and *sulphide of ammonium* did not produce a precipitate, but only after addition of *chloride of ammonium*.

tained by adding *hydrofluosilicic acid* to the hydro-
chloric acid solution of the alkaline earths.   A precipi-
tate of s i l i c o f l u o r i d e   o f   b a r i u m is produced,
which becomes visible only after the lapse of some time.

IV. REMAINING SOLUTION.

To a portion of the liquid, filtered from the precipi-
tate obtained by carbonate of ammonia, is added *phos-
phate of soda*.   A white crystalline precipitate, which
appears only after some time, indicates the presence of
m a g n e s i a.   The further examination for the fixed
alkalies depends upon the presence, or absence, of
magnesia.

a. M a g n e s i a   i s   a b s e n t.

The portion of the liquid filtered from the carbo-
nates of the alkaline earths, to which no *phosphate of
soda* has been added, is evaporated, and the residue
ignited in order to drive off the ammoniacal salts.

A portion of this residue is examined before the
blowpipe flame, a *yellow* color of the flame indicates
s o d a, a *violet* p o t a s s a, [a *red* l y t h i a]; in the two
latter cases soda is absent.

The other portion of the residue is dissolved in
water.

A portion of this solution is tested for p o t a s s a by
tartaric acid or *bichloride of platinum.*

[Another portion (if we have reason to test for
l i t h i a) is evaporated to dryness with *phosphate of
soda* and *carbonate of soda*, and the residue treated
with water.   If a crystalline salt remains, which fuses

with *carbonate of soda* upon the platinum foil in a transparent mass, l i t h i a is present.]

b. M a g n e s i a i s p r e s e n t.

The liquid is evaporated to dryness, the residue gently ignited in order to drive off the ammoniacal salts, and dissolved in water.*

To this solution is added *baryta-water*, till an alkaline reaction takes place, in order to precipitate the magnesia, which is filtered off. The excess of baryta is now separated by *ammonia* and *carbonate of ammonia* (or *sulphuric acid*), and the filtrate evaporated again to dryness. A residue remaining indicates the presence of a l k a l i e s. We proceed now as stated above.

B. DETECTION OF THE ACIDS, OR ELECTRO-NEGATIVE BODIES.

a. PRELIMINARY EXAMINATION.

The qualitative determination of acids is, if possible, still more simple than that of the bases. In almost all cases the preliminary examination of the solid (v. p. 108) as well as the nature of the base detected, directs the attention of the student to the class of acids for which he has to examine. The knowledge how a salt behaves with solvents, the reaction of the aqueous solutions on vegetable colors, is especially important in

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* If the o r i g i n a l solution is free from heavy oxides and ammoniacal salts, it may at once be employed for this purpose ; the first evaporation may then be omitted.

this respect. By heating a substance alone or with *sulphuric acid*, the presence of organic, or volatile inorganic acids may be ascertained. If in both cases we do not observe any of the characteristic phenomena mentioned in p. 110 and 113, the acid is a non-volatile inorganic acid, and belongs either to the m e t a l l i c a c i d s (a r s e n i c a c i d, a n t i m o n i c a c i d [t u n g s t i c a c i d, m o l y b d i c a c i d] c h r o m i c a c i d), to which we have been directed already, when examining for the bases, or it is s i l i c i c a c i d, b o r a c i c a c i d, p h o s p h o r i c a c i d, or s u l p h u r i c a c i d.

If we have reason to believe that various acids and their salts are present in the substance under examination, we have to consider the cases in which the preliminary examination in the dry way could give rise to deceptions; for on igniting mixtures of different salts, or treating them with sulphuric acid, phenomena may be observed, greatly differing from those which every salt would have yielded alone.

Compounds of o r g a n i c a c i d s when mixed with n i t r a t e s or c h l o r a t e s may be ignited without separation of charcoal, a deflagration, however, generally taking place; in presence of a sufficient quantity of organic matter, n i t r a t e s are completely destroyed by ignition, a carbonate being formed, if the base of the nitrate was an alkali. A mixture of a n i t r a t e and c h l o r i d e, when treated with *sulphuric acid*, evolves neither hydrochloric acid nor nitric acid, unless one of them be in great excess, but chlorine and red vapors of nitrous acid. In a mixture of a s u l p h i t e and a n i t r a t e, the s u l p h u r o u s acid is converted into sulphuric acid. S u l p h i d e s in presence of

sufficient quantities of s u l p h i t e s, c h r o m a t e s, c h l o r a t e s, etc., separate sulphur without disengagement of hydrosulphuric acid; in most of these cases s u l p h u r i c acid is formed.

In order not to overlook the presence of volatile organic acids, uncombined with bases, the acid solution is neutralised with *carbonate of soda*, evaporated and ignited ; the organic acids, which before might have been volatilised without decomposition, are now destroyed with separation of charcoal.

b. DETECTION OF THE ACIDS IN SOLUTION.

In order to detect the more important acids, the following method is employed : — In testing for acids the g e n e r a l r e a g e n t s are used in most cases only to prove the presence or the absence of an entire group of acids. The examination for the individual members of these groups requires the application of s p e c i a l r e a g e n t s. It is only necessary in a very few cases to separate an entire group of acids from a solution, in order to recognise another acid simultaneously present.

1. The presence and nature of a gaseous or volatile acid is almost generally ascertained by the preliminary treatment of the solid substance with *sulphuric acid*. C a r b o n a t e s, s u l p h i t e s, and the readily decomposable s u l p i d e s, are recognised on gently heating the substance with *hydrochloric acid*, c a r b o n i c a c i d, s u l p h u r o u s a c i d, or h y d r o s u l p h u r i c a c i d being disengaged. The two latter acids are easily distinguished by their odor, c a r b o n i c a c i d being almost inodorous. Moreover, c a r b o n i c a c i d

is indicated by soluble salts of *lime* or *baryta*, carbonates of these earths being formed; h y d r o s u l - p h u r i c   a c i d may be detected by the black metallic film, which is deposited on a paper moistened with *acetate of lead*, when brought in contact with it; a solution of s u l p h u r o u s acid is decomposed by *hydrosulphuric acid* with separation of sulphur.

2. To a portion of the n e u t r a l   s o l u t i o n   i n w a t e r *chloride of barium* is added. The precipitate, which is produced, may contain s u l p h u r i c   a c i d, [s e l e n i c   a c i d], p h o s p h o r i c   a c i d,   b o r a c i c a c i d,   s i l i c i c   a c i d,   h y d r o f l u o r i c   a c i d,   o x - a l i c   a c i d,   t a r t a r i c   a c i d,   c i t r i c   a c i d,   c h r o - m i c   a c i d,   t h e   a c i d s   o f   a r s e n i c, and different other metallic acids. The latter, as well as chromic acid, have been detected already when testing for the bases. The baryta salts of all these acids are redissolved by *hydrochloric acid* on gently heating s u l p h a t e [and s e l e n i a t e]   o f   b a r y t a excepted. The presence of these acids is therefore ascertained, if the liquid does not become completely clear on addition of *hydro-chloric* acid. Other acids are present, if the precipitate is only partially redissolved.

On neutralising the acid liquid with *ammonia*, p h o s p h a t e,   c h r o m a t e,   a n d   o x a l a t e   o f   b a - r y t a are reprecipitated; the baryta salts of the other acids, especially of b o r a c i c,   a r s e n i o u s   a n d a r s e n i c   a c i d s,   c i t r i c   a n d   t a r t a r i c   a c i d s remain in solution, unless the quantity of the ammoniacal salt formed is very small. If the compound under examination was insoluble in water, but soluble in acids, and if it contains an e a r t h   or an a l k a -

line earth, (ex. gr., p h o s p h a t e s and o x a l - a t e s of the a l k a l i n e e a r t h s, etc.,) the liquid cannot be neutralised with *ammonia* in order to test with *chloride of barium*, as on addition of *ammonia* the salt would be entirely precipitated.   The pre- sence of these compounds, however, is indicated al- ready by *sulphide of ammonium* when testing for the bases.   If the acids mentioned are united with an ox- ide precipitable in form of a sulphide by *hydrosulphuric acid*, or *sulphide of ammonium*, the detection becomes far easier after the separation of the metal.

3. To another portion of the original n e u t r a l so- lution (if it be acid we must neutralise it by *ammonia*, if alkaline by *nitric acid*) is added *nitrate of silver*. By this reagent h y d r o c h l o r i c, h y d r o b r o m i c, h y d r i o d i c, h y d r o c y a n i c, and h y d r o s u l - p h u r i c a c i d s are precipitated, and also p h o s - p h o r i c, c h r o m i c, b o r a c i c, s i l i c i c, o x a l i c, t a r t a r i c, and c i t r i c a c i d s.   On addition of di- lute *nitric acid*, all these precipitates are dissolved, c h l o r i d e, b r o m i d e, i o d i d e, and c y a n i d e of s i l v e r excepted.   Most of the silver compounds dis- solved in this way may be reprecipitated by carefully neutralising with *ammonia*, if the quantity of the am- moniacal salt formed is not too large.

If the solution contains a soluble s u l p h i d e, or free h y d r o s u l p h u r i c a c i d, before testing with *nitrate of silver* it is necessary to separate all the hydrosulphuric acid by gently heating the solution acidulated with *nitric acid*.

The curdy silver precipitate insoluble or soluble in

nitric acid is washed and digested with *ammonia*, by which c h l o r i d e and c y a n i d e of s i l v e r are readily dissolved; b r o m i d e of s i l v e r is more difficultly soluble, i o d i d e of s i l v e r is almost insoluble.

If a sufficient quantity of the original liquid is at hand, we may test for each of these acids separately, availing ourselves of the reactions given in the second section (p. 81, etc.). If, however, only the silver precipitate is at our disposal, it is digested with *ammonia*, and the solution filtered off from the residue (i o d i d e of s i l v e r); the silver compounds dissolved in ammonia are then reprecipitated by *nitric acid*, washed with water, dried and fused in a porcelain crucible. C y a n i d e of s i l v e r is decomposed on fusion, metallic silver, or a subcyanide remaining behind; upon the residue we place a piece of metallic *zinc*, and pour over it a small quantity of *dilute pure sulphuric acid;* in this way we obtain after some time a solution of c h l o r i d e and b r o m i d e of z i n c. Of this solution a portion is agitated with *ether* and *chlorine water* (*hydrochloric acid* and *hypochlorite of lime*); if b r o m i n e is present, the ether assumes a yellowish-brown color; if not, and another portion of the solution yields a curdy precipitate with *nitrate of silver*, the presence of c h l o r i n e is proved. In order to detect c h l o r i d e s in presence of a great excess of b r o - m i d e s and i o d i d e s, the original substance is distilled in a small retort with *chromate of potassa* and *concentrated sulphuric acid*. On addition of *ammonia* the r e d d i s h brown distillate becomes yellow if c h l o r i n e was present, whilst in the presence of

bromides and iodides only, the color disappears altogether.

4. If by the preliminary examination we have ascertained that a *non-volatile organic acid* is present, the aqueous solution is to be mixed with *ammonia, chloride of ammonium* and *chloride of calcium.* If *ammonia* produces a precipitate, this must be filtered off before adding the *chloride of calcium.* Of organic acids *chloride of calcium* precipitates in the cold oxalic acid and tartaric acid, of inorganic acids a precipitate may be obtained of *sulphuric acid* (if the solution be concentrated enough) phosphoric acid and hydrofluoric acid, the presence of which has been indicated already by *chloride of barium* and *nitrate of silver.* If oxalic acid be present, the original solution containing an excess of ammonia, gives a white precipitate with *sulphate of lime*, which is insoluble in *acetic acid*, but dissolves readily in *nitric acid* and *hydrochloric acid.* The presence of tartaric acid is ascertained by treating with *potassa* in the cold, the precipitate obtained by *chloride of calcium and ammonia*, after it has been washed and filtered off. If the precipitate consists entirely of tartrate of lime, it is completely redissolved; in case, however, a residue is left (oxalate or phosphate of lime, fluoride of calcium), the potassa solution is filtered off and boiled for some time. Tartrate of lime, is reprecipitated in this manner.

Citric and [malic] acids, if present, are contained in the liquid filtered off from the precipitate, which *chloride of calcium* and *ammonia* produced. The lime salts of these acids may be precipitated

from this liquid by *alcohol*, n i t r a t e o f l i m e also
by ebullition. We must observe in this case, that if
s u l p h u r i c acid be present *alcohol* produces always
a precipitate of s u l p h a t e o f l i m e, which however
by its comportment when ignited cannot be confound-
ed with c i t r a t e and m a l a t e o f l i m e. If a salt
of these organic acids, and especially of o x a l i c and
t a r t a r i c a c i d is to be examined, which is insolu-
ble in water but dissolves in acids, the process for
ascertaining them above described cannot be used, as
from an acid solution the salt is entirely reprecipitated
on addition of *ammonia*.   In this case the organic acid
of these salts insoluble in water is easily withdrawn by
boiling with *carbonate of potassa*, or *carbonate of soda*.
We have now a salt soluble in water, the acid of
which may be easily ascertained by neutralising the
liquid with *hydrochloric acid*, and following the course
above explained.

The presence of s u l p h u r i c [and s e l e n i c] acid
has been indicated by the *baryta precipitate*, insoluble
in *hydrochloric acid*.

For p h o s p h o r i c a c i d we test separately by
adding to the original aqueous solution a mixture of
sulphate of magnesia, *chloride of ammonium* and *am-
monia*, by which a precipitate of p h o s p h a t e o f
m a g n e s i a and a m m o n i a is obtained; if the salt
was insoluble in water, but soluble in acids, to the acid
solution a sufficient quantity of *acetate of ammonia*,
and a few drops of *sesquichloride of iron* are added, by
which p h o s p h a t e o f s e s q u i o x i d e o f i r o n,
nsoluble in *acetic acid*, is precipitated.

Also for h y d r o f l u o r i c a c i d we test separately

by heating gently a portion of the dry original substance with *concentrated sulphuric acid* in a platinum crucible. Vapors of h y d r o f l u o r i c a c i d in this manner are disengaged, which act on glass. (Compare hydrofluoric acid, p. 86.)

5. The fourth group of acids consists of s u c c i n i c a c i d, b e n z o i c a c i d, a c e t i c a c i d, and f o r m i c a c i d, the presence of which is indicated by their behavior with *sesquichloride of iron*. These acids are distinguished from each other in the following ways. To the n e u t r a l aqueous solution *sesquichloride of iron* is added (p h o s p h o r i c a c i d, if present, must first be separated either by *chloride of calcium* and *ammonia*, or by *sulphate of magnesia*, *chloride of ammonium*, and *ammonia*). If *sesquichloride of iron* produces a precipitate, succinic acid or benzoic acid, or both, are present. In this case we now test the rather concentrated original solution for b e n z o i c and s u c - c i n i c acid by addition of an *acid* or *chloride of barium* and *alcohol* (v. p. 104), or we separate the organic acid from the iron precipitate by digestion with *ammonia*, and test the filtrate containing the ammoniacal salts of the organic acids.

A c e t i c and f o r m i c acid, when existing in the form of salts assume a red color when with mixed *sesquichloride of iron*. We ascertain the presence of the former by evaporating the original solution (if it is acid it must be neutralised first), and heating the residue left with a mixture of *sulphuric acid* and *alcohol* in a test-tube. A c e t i c e t h e r is formed, and is easily distinguished by its odor. Or we distil the residue with moderately *dilute sulphuric acid*, and digest the

distillate with *oxide of lead* in excess. Tribasic acetate of lead is formed, which possesses an alkaline reaction.

The presence of formic acid is ascertained by boiling the original solution with *nitrate of silver* or with *oxide of mercury*. Both oxides are reduced to the metallic state with evolution of carbonic acid. *Chloride of mercury* is generally first reduced to subchloride, which by boiling is converted into metal.

The presence of nitric acid, chloric acid, etc., is always indicated by the preliminary examination of the original substance. By its behavior with *sulphuric acid* in the presence of metallic *copper*, or with *protosulphate of iron*, nitric acid may be easily distinguished from chloric acid, the salts of which yield a dark yellow gas, when treated with *sulphuric acid.* Moreover the alkaline chlorates on being heated yield chlorides with disengagement of oxygen.

Boracic acid may be easily overlooked in the preceding experiments, as most of its salts are very soluble, especially in ammoniacal salts. It is therefore necessary to make a separate experiment for its detection, if we have reason to suspect its presence. For this purpose the original substance, or a concentrated solution of it, is mixed with *sulphuric acid* and *alcohol*, and the latter kindled. In presence of boracic acid the flame assumes a fine green color, which becomes visible more especially in the latter stage of the experiment.

The presence of silicic acid is always indicated by the results of the preliminary examination ; in its insoluble modification it occurs principally in minerals

and artificial silicates (glasses, etc.); the soluble modification exists in mineral waters, in alkaline silicates, etc. In all these cases it is necessary to reconvert the soluble modification (which from silicates undecomposable by acids is obtained by fusion with *alkaline carbonates*) into the insoluble one. This is effected by evaporating with an excess of *hydrochloric acid*. If no residue remains, which is insoluble in *hydrochloric acid*, the absence of silicic acid is proved. If a residue remains it is examined with *phosphorus salt* or *carbonate of soda*, as explained above.

TABLE I.

BEHAVIOR

OF SOLUTIONS OF THE METALS WITH HYDROSULPHURIC ACID, SULPHIDE OF AMMONIUM AND CARBONATE OF AMMONIA, EMPLOYED SUCCESSIVELY.

ELEMENTS PRECIPITATED FROM THEIR ACID SOLUTION BY HYDROSULPHURIC ACID AS SULPHIDES.		BODIES PRECIPITATED BY SULPHIDE OF AMMONIUM.			BODIES NOT PRECIPITATED BY HYDROSULPHURIC ACID OR SULPHIDE OF AMMONIUM. IN THE PRESENCE OF CHLORIDE OF AMMONIUM ON ADDITION OF CARBONATE OF AMMONIA ARE	
Soluble in sulphide of ammonium and reprecipitated by hydrochloric acid:	*Insoluble in sulphide of ammonium:*	*As sulphides:*	*As oxides:*	*As salts:*	PRECIPITATED:	NOT PRECIPITATED.
Antimony — orange Arsenic ⎫ Tin ⎬ . . . yellow ⎭ Gold ⎫ Platinum ⎬ . . . black [Iridium] ⎭ [Selenium] . . . reddish [Tellurium] . . . black [Molybdenum] . . brown	Mercury ⎫ Silver ⎬ . black Lead ⎬ or Bismuth ⎬ brownish- Copper ⎭ black. Cadmium . . . yellow [Palladium] ⎫ [Rhodium] ⎬ brownish- [Osmium] ⎭ black.	Nickel ⎫ Cobalt ⎬ . . . black Manganese . . flesh-colored Iron . . . . black Zinc . . . . white [Uranium] . . brownish-black.	Alumina ⎫ soluble [Glucina] ⎬ in Sesquioxide of Chromium ⎭ potassa [Thorina] ⎫ [Yttria] ⎬ [Oxide of Cerium] ⎬ insoluble [Zirconia] ⎬ in [Titanic acid] ⎬ potassa [Tantalic acid] ⎭	Baryta Strontia Lime ⎱ in combination with phosphoric acid, oxalic acid, boracic acid, hydrofluoric acid Magnesia ⎱ in combination with phosphoric acid	Baryta Strontia Lime	Magnesia Potassa Soda [Lithia] Ammonia

Tungsten cannot be precipitated by *hydrosulphuric acid*, as tungstic acid never exists in a nitric or hydrochloric acid solution. Compare what is said of the compounds of tungsten, molybdenum, and vanadium, p. 63, and the following.

TABLE II.

PRECIPITATE PRODUCED BY HYDROSULPHURIC ACID.

a. PORTION SOLUBLE IN SULPHIDE OF AMMONIUM.

THE solution obtained by treating the precipitate with *sulphide of ammonium* is filtered off from the insoluble residue (*b*) and saturated with a slight excess of *hydrochloric acid*. If the cloudiness produced is white, it probably arises but from s u l p h u r; if a yellow or orange precipitate is produced, it may contain a r s e n i c, t i n, or a n t i m o n y. The precipitate is then to be treated according to p. 58, and the original solution tested for these metals. If the sulphide precipitated by hydrochloric acid possesses a darker color, it is to be investigated for the other bodies of this group, g o l d, p l a t i n u m, [i r i d i u m, s e l e n i u m, t e l l u r i u m, m o l y b d e n u m]. From the results of the preliminary investigation, especially from their behavior with solvents, the probable presence of the individual members is to be inferred.

b. PORTION INSOLUBLE IN SULPHIDE OF AMMONIUM.

The precipitate is boiled with concentrated *nitric acid*. A black residue remaining undissolved consists of s u l p h i d e   o f   m e r c u r y.* The formation of a white precipitate points out the presence of lead, which is also partly contained in the solution. This solution is diluted with water and mixed with *hydrochloric acid*.

WHITE PRECIPITATE: Chloride of silver, subchloride of mercury, chloride of lead. *The precipitate is treated with a great amount of water.*			FILTRATE: Oxide of lead, teroxide of bismuth, oxides of copper, cadmium, [and palladium]. *Ammonia is added in excess.*				
RESIDUE: Chloride of silver, subchloride of mercury. *Treatment with ammonia.*		FILTRATE: Chloride of lead. Lead is also found in the solution filtered off from the precipitate obtained by *hydrochloric acid*.	PRECIPITATE:		FILTRATE.		
RESIDUE: Black suboxide of mercury. If the residue is white the chloride of lead was not completely dissolved, and suboxide of mercury cannot be present.	FILTRATE: Chloride of silver is precipitated by *nitric acid*.		Oxide of lead. Confirmatory test. Precipitable by *dilute sulphuric acid*.	Teroxide of bismuth. Confirmatory test. Precipitable by *water* on sufficient evaporation of the solution.	Oxide of copper. Blue color of the ammoniacal solution. Brownish-red precipitate of the acid solution with *ferrocyanide of potassium*.	Oxide of cadmium. The ammoniacal solution is neutralised by *hydrochloric acid* and precipitated by *carbonate of ammonium*.	[Oxide of palladium.] The brown or reddish-brown solution in *nitric acid* is discolored by *ammonia*. *Iodide of potassium* produces a black precipitate.

* In this table we have mentioned s u b c h l o r i d e   o f   m e r c u r y as a member of the group precipitated by *hydrochloric acid* from the nitric acid solution of the precipitate obtained by *hydrosulphuric acid*, although s u l p h i d e   o f   m e r c u r y is insoluble in nitric acid, and a solution of this sulphide in nitro-hydrochloric acid contains always the chloride. Generally however, the three insoluble chlorides are separated from the liquid by hydrochloric acid, before treating the original solution by hydrosulphuric acid. If, therefore, we find mercury in the precipitate obtained by hydrosulphuric acid, we may conclude that it was present in the solution in the form of oxide.

In order to ascertain in what state t i n, or a r s e n i c, is contained in a liquid, we must examine the original solution. We have omitted the oxides of osmium and rhodium, as they occur only in platinum ores, in examining which particular attention is to be paid to these metals.

TABLE III.

PRECIPITATE PRODUCED BY SULPHIDE OF AMMONIUM,

Treated with dilute hydrochloric acid and gently heated; the black residue examined before the blowpipe for cobalt.
Boiled with nitro-hydrochloric acid; the whole dissolved.

Addition of an excess of potassa in the cold.

FILTRATE:
Oxide of Zinc, Alumina, [Glucina], Sesquioxide of Chromium.

PRECIPITATE.
Oxide of Nickel, Oxide of Cobalt, Oxide of Manganese, Sesquioxide of Iron, [Sesquioxide of Uranium, Oxide and Sesquioxide of Cerium, Thorina, Yttria, Zirconia, Titanic acid, Tantalic acid, ‡] and when in combination with oxalic, phosphoric, boracic, or hydrofluoric acids, Baryta, Strontia, Lime, also Magnesia, when in combination with phosphoric acid.

Continuous boiling of the alkaline solution.

Solution of the washed precipitate in nitro-hydrochloric acid.
Addition of chloride of ammonium and ammonia.

FILTRATE:
Oxide of Zinc, Alumina, [Glucina.]

PRECIPITATE:
Sesquioxide of Chromium.*

FILTRATE:
Oxides of Cobalt, Nickel, Manganese.

PRECIPITATE:
Sesquioxide of Iron, [Sesquioxide of Uranium, Oxide and Sesquioxide of Cerium, etc.]; and when in combination with oxalic, phosphoric, boracic, or hydrofluoric acid, Baryta, Strontia, Lime; also phosphate of Magnesia.

Addition of hydrosulphuric acid.

The solution is slightly acidulated with acetic acid, treated with hydrosulphuric acid, and gently heated.

Digestion with a concentrated solution of carbonate of ammonia.

FILTRATE:
Alumina. † [Glucina.]
Saturation with hydrochloric acid, addition of ammonia, and digestion of the precipitate produced in carbonate of ammonia.

PRECIPITATE:
Sulphide of Zinc.

FILTRATE:
Oxide of Manganese.

Supersaturation with ammonia and addition of sulphide of ammonium.

PRECIPITATE ·
Sulphide of Manganese.

Examination with carbonate of soda on platinum-foil.

PRECIPITATE:
Sulphide of Nickel. Sulphide of Cobalt.
Examination for nickel with cyanide of potassium in the nitro-hydrochloric acid solution.

FILTRATE:
[Sesquioxide of Uranium and some Oxide of Cerium, etc.:]
A yellow color of the solution and the precipitate obtained by boiling shows the presence of Sesquioxide of Uranium.
Examination before the blowpipe.
Examination for Oxide of Cerium with sulphate of potassa.

RESIDUE:
Sesquioxide of Iron, [Oxide of Cerium, etc.] Baryta, Strontia, Lime, when in combination with oxalic, phosphoric, boracic, or hydrofluoric acids; also phosphate of magnesia.
The hydrochloric acid solution is tested,—
For sesquioxide of iron, by *ferrocyanide of potassium.*
For phosphoric acid, by *sesquichloride of iron* and *acetate of ammonia.*
For oxalic acid, by *chloride of calcium* and *acetate of ammonia.*
For hydrofluoric acid, by *sulphuric acid.*
With respect to the detection of the bases, *vide* p. 9.

FILTRATE:
[Glucina.]
Precipitation by boiling. Examination before the blowpipe.

RESIDUE:
Alumina.
Examination before the blowpipe.

* Sesquioxide of chromium and sesquioxide of iron, when in company, affect their respective reactions according to their relative quantities. If a very large amount of sesquioxide of chromium is present, small quantities of sesquioxide of iron dissolve completely in *potassa*; in the presence of much sesquioxide of iron, sesquioxide of chromium is quite insoluble in *potassa*. Both oxides may, however, be easily separated on fusion with *nitrate of potassa* and *carbonate of soda*.

† Phosphate of alumina comports itself with *sulphide of ammonium*, with *chloride of ammonium*, and with *potassa* in the same manner as pure alumina.

‡ The presence of tantalic and titanic acid and the earths insoluble in potassa is not taken into account in this table; if a preliminary investigation points out the presence of one of these oxides, a comparison of their behavior with reagents will indicate a method for their qualitative determination.

TABLE IV.

BEHAVIOR

OF THE MORE IMPORTANT ACIDS, INORGANIC AND ORGANIC, ON HEATING THEIR SALTS WITH SULPHURIC ACID.

INORGANIC ACIDS.			ORGANIC ACIDS.	
ACIDS VOLATILE.		ACIDS NON-VOLATILE, OR VOLATILE ONLY AT HIGH TEMPERATURES.	VOLATILE ACIDS.	NON-VOLATILE ACIDS.
WITHOUT DECOMPOSITION.	WITH DECOMPOSITION.			

Carbonic acid. Inodorous; precipitates lime-water.
 	
Sulphurous acid. Odor of burning sulphur; is decomposed by hydrosulphuric acid with separation of sulphur.
 	
Hydrosulphuric acid. Odor of rotten eggs; black precipitate with lead salts.
 	
Hydrochloric acid. Acid vapor fuming in contact with air.
 	
Hydrofluoric acid. Etches glass.
 	
Nitric acid. Colorless acid gas; in presence of copper-turnings red vapors.
	Hydriodic acid. Violet vapors of iodine.
	
	Hydrobromic acid. Brown vapors of bromine.
	
	Hydrocyanic acid. Disengagement of carbonic oxide, which burns with a blue flame. With dilute sulphuric acid hydrocyanic acid is evolved. Compounds of *ferrocyanogen* and *ferricyanogen* exhibit similar reactions.
	
	Chloric acid. Dark-yellow gas.
	
	Hydrosulphocyanic acid. Disengagement of hydrocyanic acid and precipitation of a yellow powder.
	
	Hypochlorous acid. Yellowish-green gas, chlorine.
	
	Bromic acid. Brown vapors of bromine and oxygen.
		Silicic acid.
		
		Boracic acid.
		
		Phosphoric acid.
		
		Metallic acids. These are found when testing for the bases.
		
		Sulphuric acid.
		
		[*Selenic acid.*]
		
		Chromic acid. Evolution of oxygen, when treated with concentrated sulphuric acid.
			Formic acid. Evolution of pure carbonic oxide.
			
			Acetic acid. Evolution of acetic acid; in presence of alcohol of acetic ether.
			
			Benzoic acid
			       and
			Succinic acid
			  are not decomposed by sulphuric acid.
				Oxalic acid. Is decomposed into carbonic acid and carbonic oxide without separation of charcoal.
				
				Tartaric acid,
				
				[*Racemic acid,*]
				
				Citric acid,
				
				[*Malic acid,*]
				  as most other organic acids, are decomposed by concentrated sulphuric acid, with separation of charcoal; carbonic acid, carbonic oxide, and sulphurous acid being disengaged.

TABLE V.

BEHAVIOR

OF THE MORE IMPORTANT ACIDS, INORGANIC AND ORGANIC, WITH CHLORIDE OF BARIUM, NITRATE OF SILVER, CHLORIDE OF CALCIUM, AND SESQUICHLORIDE OF IRON.

CHLORIDE OF BARIUM precipitates:	NITRATE OF SILVER precipitates:	CHLORIDE OF CALCIUM precipitates:	SESQUICHLORIDE OF IRON.	
a. From neutral solutions, the precipitate being soluble in hydrochloric or nitric acid. *Sulphurous acid* *Carbonic acid* *Phosphoric acid* *Silicic acid* *Hydrofluoric acid* *Oxalic acid* } white *Boracic acid* *Tartaric acid* *Citric acid* *Arsenic acid* *Arsenious acid* * *Chromic acid* . . yellow b. From neutral and acid solutions, the precipitates being insoluble in hydrochloric and nitric acid. *Sulphuric acid* } white [*Selenic acid*] Seleniate of baryta disengages chlorine, when boiled with hydrochloric acid, selenious acid being formed.	a. From neutral solutions, the precipitate being soluble in nitric acid. *Phosphoric acid* . yellow or white *Boracic acid* . . white *Silicic acid* . . white *Chromic acid* . . red *Oxalic acid* *Tartaric acid* } white *Citric acid* *Arsenic acid* . . brown *Arsenious acid* . . yellow b. From neutral and acid solutions, the precipitate being insoluble or difficultly soluble in nitric acid. *Iodic acid*, the original salt detonates with ignited charcoal. *Hydrochloric acid*, white precipitate, soluble in ammonia. *Hydrobromic acid*, precipitate difficultly soluble in ammonia. *Hydriodic acid*, yellow precipitate, nearly insoluble in ammonia. *Hydrocyanic acid*, white precipitate, which decomposes when heated, and disengages hydrocyanic acid when moistened with hydrochloric acid. *Hydrosulphocyanic acid*, white curdy precipitate, difficultly soluble in ammonia. *Hydrosulphuric acid*, black precipitate. *Sulphurous acid* } On heating, reduce *Formic acid* } nitrate of silver.	From neutral solutions; also in the presence of ammoniacal salts or free ammonia. *Sulphuric acid*, from solutions not too dilute; completely by addition of alcohol. *Phosphoric acid*, white precipitate, soluble in acetic acid, when freshly thrown down. *Hydrofluoric acid*, white precipitate, insoluble in acetic acid, and partly soluble in hydrochloric acid. *Oxalic acid*, white precipitate, insoluble in acetic acid. *Tartaric acid*, white precipitate, soluble in cold potassa, and reprecipitated by boiling. *Citric acid*, the precipitate is produced only by boiling, and is insoluble in potassa.	a. Precipitates from perfectly neutral solutions. *Succinic acid* } *Benzoic acid* } light brown b. Imparts a reddish-brown color or to the neutral solutions of *Hydrosulphocyanic acid*, *Acetic acid*, and *Formic acid*. ### SPECIAL REACTIONS. *Benzoic acid* may be recognised by being separated from concentrated solution of its salts — by means of an acid. *Hydrosulphocyanic acid* gives a yellow precipitate, when boiled with dilute sulphuric acid. *Acetic acid* is distinguished by the formation of acetic ether, and the basic lead-salt. *Formic acid* is recognised by its property of reducing nitrate of silver.	Acids which are not precipitated: *Nitric acid*, *Chloric acid*. The salts of these acids deflagrate on ignited charcoal. ### REMARKS. In case the presence of a group of acids is pointed out by general reagents, the individual member is always to be recognised by the special reactions given in the second section of this book. These special reactions will serve not only to confirm the results of the general reagents, but allow us also to distinguish different acids, when present together. For *boracic acid*, *silicic acid*, and *hydrofluoric acid*, special experiments are always to be made.

* *Boracic, tartaric, citric, arsenic,* and *arsenious acids,* are not precipitated in the presence of ammoniacal salts.